

Proceedings of the Indian Academy of Sciences (Chemical Sciences)

Volume 99, 1987

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Special issue on Trends in Theoretical Chemistry

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Foreword

The First National Meeting on Trends in Theoretical Chemistry (1986) was the forerunner of a series of unusual scientific conferences in which creativity and spontaneity are sought to be stimulated amid nature's splendour, according to an Indian tradition. Sponsored by the Indian Academy of Sciences, Bangalore and the Chemistry Department, Panjab University, Chandigarh, the purpose of the Meeting was to bring together Indian theoretical chemists, especially those of the younger generation, in order to foster intense discussions on one another's area of study, eventually leading to a focussing of attention on emerging problems of importance vis-a-vis the world scene in theoretical chemistry. The format of the Meeting was as follows: pre-lunch formal presentations of research papers by the participants, post-lunch to pre-dinner informal outdoor discussions in natural surroundings and after-dinner talks; there was also a concluding panel discussion on theoretical chemistry in India. Apart from chemists, the total of about thirty five participants had also physicists, biophysicists, and mathematicians. On an average, the daily scientific programme consumed about twelve hours including the time devoted to cooperative interaction among the participants.

The papers published in these proceedings provides a glimpse into some of the interesting areas of theoretical chemistry being pursued in India. The list is not exhaustive and it is hoped that future proceedings of such Meetings would bring forth greater variety and sophistication.

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Wigner-Weisskopf atom and quantum Stochastic dilations

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Abstract. Quantum stochastic processes are operator processes in Fock space adapted in a natural way with respect to the tensor product factorization of the space. One can describe the usual classical stochastic processes (e.g., Brownian, Poisson) as well as new variety of non-commuting processes in this language. In this framework, quantum stochastic calculus (like Ito calculus in the classical case) has been developed by Hudson and Parthasarathy. Using this calculus, one can rewrite the simple Wigner-Weisskopf model of a decaying atom. In this model, the system (atom) is coupled linearly to the environment (a bath of infinite degrees of freedom represented by a reducible bosonic quantum stochastic process at non-zero temperature). The quantum stochastic differential equation of evolution is solved, and the bath variables are averaged out by taking vacuum expectation values leading to a law of relaxation of the state of the system.

Keywords. Quantum stochastic calculus; two-level atom; singular coupling limit.

1. Introduction

Examples of unstable systems or relaxation models abound in nature, e.g., decaying particles, radiation of an excited atom, measurement process in quantum mechanics and relaxation of a macrosystem to its equilibrium, to name a few. All these examples have a unifying backdrop, viz., there is a system where our interest lies and there is an environment or bath or apparatus. In a suitable sense the environment is 'large' compared to the system and the two are 'coupled'.

Almost all attempts to understand such phenomena in the quantum mechanical framework can be divided into two broad categories. The first is model-independent general analysis and has been summarized in the recent book of Exner (1985). The second is a somewhat more detailed, sometimes model-dependent study, typical examples of which are the works of Fonda *et al* (1973), Davies (1976), and Gorini *et al* (1976).

In the second group, one usually takes a Hamiltonian consisting of a part as the Hamiltonian of the system, and another for the environment and then the so-called coupling or interaction Hamiltonian. The Schrödinger or Heisenberg equation is then written down and in an appropriate weak coupling or singular coupling limits, the irreversible master equation results. Typically this involves a rescaling of time and one usually argues that the time scale of observation is very large compared to the intrinsic time-scale of relaxation of the system so that one has the final effect of wiping out the memory terms inherent in the original equations of motion.

More recently one has a new theory, that of the quantum stochastic processes, pioneered by Hudson and Parthasarathy (1984) and Accardi (1980), which allows one to describe the situation more satisfactorily though the general theory of relaxation phenomena is still missing. We shall be content here with a brief description of the simple Wigner-Weisskopf two-level atom, 'stochastically' coupled to the radiation field basing on the work of Applebaum (1986).

2. The model

The model is that of a two-level atom represented by $\mathcal{C}^2$ with the algebra of observables $M_2(\mathcal{C})$ generated by $a = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$ and $a^\dagger = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$ so that the CAR (canonical anti-commutation relations) are satisfied:

$$a^2 = 0, aa^\dagger + a^\dagger a = I. \quad (1)$$

The atomic Hamiltonian H_S :

$$H_S = \frac{1}{2} w_0 (a^\dagger a - a a^\dagger), \quad w_0 > 0, \text{ and}$$

its Gibbs state at inverse temperature $\beta > 0$ is given by the density matrix

$$\begin{aligned} \rho_S &= [\text{tr} \exp(-\beta H_S)]^{-1} \exp(-\beta H_S) \\ &= [\exp(1/2 \beta w_0) + \exp(-1/2 \beta w_0)]^{-1} \begin{bmatrix} \exp(1/2 \beta w_0) & 0 \\ 0 & \exp(-1/2 \beta w_0) \end{bmatrix}. \end{aligned} \quad (2)$$

The bath or the environment of the atom is composed of n independent harmonic oscillators, generated by $\{a_j, 1 \leq j \leq n\}$ satisfying the CCR (canonical commutation relations)

$$[a_j, a_k] = 0, [a_j, a_k^\dagger] = \delta_{jk} I. \quad (3)$$

The Hamiltonian for the environment H_E is given as $H_E = \sum_{j=1}^n w_j a_j^\dagger a_j$

($w_j > 0$), and the associated state by the density matrix $\rho_E = [\text{tr} \exp(-\beta H_E)]^{-1} \exp(-\beta H_E)$. Then it is easy to see that

$$\text{tr}(a_j \rho_E) = \text{tr}(a_j^\dagger \rho_E) = 0, \text{tr}(\rho_E a_j^\dagger a_k) = \delta_{jk} \mu_j^2,$$

where

$$\mu_j^2 = [1 - \exp(-\beta w_j)]^{-1} \exp(-\beta w_j) > 0.$$

Following Araki and Woods (1963) (see also Parthasarathy and Sinha 1986), we write the cyclic *-representation (though reducible) on $\mathcal{H}_n = r(\mathcal{C}^n) \otimes r(\mathcal{C}^n)$ as follows.

$$B_j = \lambda_j b^{(1)}(e_j) \otimes I^{(2)} + \mu_j I^{(1)} \otimes b^{(2)}(e_j),$$

where

$$\lambda_j^2 = 1 + \mu_j^2,$$

and $b^{(i)}(e_j)$ ($i = 1, 2$) are two copies of the canonical (zero temperature) irreducible Fock representation of CCR in $r(\mathcal{C}^n)$, the Fock space over $\mathcal{C}^n$. The cyclic vector is $\Omega \otimes \Omega$, where Ω is the vacuum vector in $r(\mathcal{C}^n)$ so that

$$\begin{aligned} [B_j, B_k] &= \delta_{jk}, \\ \langle \Omega \otimes \Omega, B_j^\dagger B_k \Omega \otimes \Omega \rangle &= \mu_j^2 \delta_{jk}. \end{aligned} \quad (4)$$

The B_j 's are the finite temperature (reducible) representation of the CCR of finite degrees of freedom.

The states of the total system is described by vectors in $\mathcal{C}^2 \otimes H_n$ and the interaction Hamiltonian by

$$H_I = \sum_{j=1}^n g_j (\varepsilon a + \eta a^\dagger) B_j + \bar{g}_j (\varepsilon a^\dagger + \eta a) B_j^\dagger, \quad (5)$$

with $\varepsilon, \eta \geq 0$, and $g_j \in \mathcal{C}$. The total Hamiltonian $H = H_S + H_E + H_I = H_0 + H_I$ is clearly self-adjoint since B_j is bounded relative to $B_j^\dagger B_j$.

In the interaction representation in $\mathcal{C} \otimes H_n$, set $W(t) = \exp(iH_0 t) \exp(-iH t)$ so that a simple calculation leads to

$$\frac{dW(t)}{dt} = -ik(t) W(t),$$

$$\begin{aligned} \text{where } K(t) &= [\varepsilon a \exp(-iw_0 t) + \eta a^\dagger \exp(iw_0 t)] F(t) \\ &+ [\varepsilon a^\dagger \exp(iw_0 t) + \eta a \exp(-iw_0 t)] F^\dagger(t), \text{ with} \end{aligned}$$

$$F(t) = \sum_{j=1}^n g_j \exp(-iw_j t) B_j. \quad (6)$$

It then follows easily from (4) and (6) that

$$[F(s), F(t)] = 0, [F(s), F(t)^\dagger] = \sum_{j=1}^n |g_j|^2 \exp[-iw_j(s-t)],$$

$$\text{and } \langle \Omega \otimes \Omega, F(s)^\dagger F(t) \Omega \otimes \Omega \rangle$$

$$\begin{aligned} &= \sum_{j,k} \bar{g}_j g_k \exp[i(w_j s - w_k t)] \operatorname{tr} \rho_E a_j^\dagger a_k \\ &= \sum_j |g_j|^2 \mu_j^2 \exp[-iw_j(t-s)]. \end{aligned} \quad (7)$$

Formally the solution of (5) can be written down as either a time-ordered exponential series of whose convergence we cannot say much or as a continuous product integral. For a partition $0 = t_0 < t_1 < t_2 \dots t_n = t$ with $\Delta_j = t_{j+1} - t_j$, we can formally write

$$W(t) = \lim_{|\Delta_j| \rightarrow 0} \prod_{j=1}^n \exp [-ik(t_j) \Delta_j]. \quad (8)$$

3. Singular coupling limit or Wigner-Weisskopf approximation and quantum stochastic differential equation

Now we suppose that in the limit of the degree of freedom $n \rightarrow \infty$ the frequencies w_j are uniformly distributed over IR and $|g_i|^2$ are all close to 1. Then formally (still denoting the formal limit of F by the same symbol F)

$$[F(t)] = 0, [F(s), F(t)^\dagger] = \delta(s-t)$$

$$\text{and } \langle \Omega \otimes \Omega, F(s)^\dagger F(t) \Omega \otimes \Omega \rangle = \int dw \mu(w)^2 \exp [-iw(t-s)],$$

where $\mu(w)^2 = [\exp(\beta w) - 1]^{-1}$. With a further simplifying assumption that $\mu(w)$ is a constant $= \mu_0^2 = [\exp(\beta w_0) - 1]^{-1}$, the above looks like

$$\langle \Omega \otimes \Omega, F(s)^\dagger F(t) \Omega \otimes \Omega \rangle = \mu_0^2 \delta(s-t). \quad (9)$$

Mathematically meaningful objects satisfying (9) can be realized by introducing the 'smeared fields' for $f, g \in L^2(IR)$,

$$A(f) \equiv \int F(t) \bar{f}(t) dt, \quad A^\dagger(g) = \int F(t)^\dagger g(t) dt$$

leading to $[A(f), A^\dagger(g)] = \int \bar{f}(s) g(s) ds$. If we write $A(t) \equiv A(\chi_{[0,t]})$ and $A^\dagger(t) = A^\dagger(\chi_{[0,t]})$, then the exponent in the RHS of (8) can be expressed as:

$$\begin{aligned} -ik(t) dt &= G(t)^\dagger F(t) dt - G(t) F^\dagger(t) dt \\ &= G(t)^\dagger dA(t) - G(t) dA^\dagger(t), \end{aligned}$$

with $G(t) = i[\epsilon a^\dagger \exp(iw_0 t) + \eta a \exp(-iw_0 t)]$. Thus (8) formally looks like

$$W(t) = \lim \prod_{j=1}^n \exp [G(t)^\dagger dA(t) - G(t) dA^\dagger(t)].$$

This form of $W(t)$ can be given a precise meaning in the context of quantum Ito integral or quantum stochastic differential equation as in Hudson and Parthasarathy (1982, 1984), viz.,

$$\begin{aligned} dW(t) &= W(t) \{G(t)^\dagger dA(t) - G(t) dA^\dagger(t) \\ &\quad - \frac{1}{2} [\lambda_0^2 G(t)^\dagger G(t) + \mu_0^2 G(t) G(t)^\dagger] dt\} \end{aligned} \quad (10)$$

with initial value $W(0) = I$, and $\lambda_0^2 = 1 + \mu_0^2$. Here we have used the notations of Hudson and Parthasarathy (1984) (see also Sinha 1986), with the proviso that the Ito product looks like: $dA dA^\dagger = \lambda_0^2 dt$, $dA^\dagger dA = \mu_0^2 dt$.

We rewrite (10) in terms of $U(t) = \exp(-iH_S t) W(t)$ as

$$dU = U \{G^\dagger dA - G dA^\dagger - [iH_S + \frac{1}{2} (\lambda_0^2 G^\dagger G + \mu_0^2 G G^\dagger)] dt\},$$

where

$$G = G(0) = i(\epsilon a + \eta a). \quad (11)$$

We can instead look at the effect of this evolution on the system observables in $M_2(\mathcal{C})$ and find that for $X \in M_2(\mathcal{C})$ if we write

$$T_t(X) = \langle \cdot \otimes (\Omega \otimes \Omega), U(t) X U(t)^\dagger \cdot \otimes (\Omega \otimes \Omega),$$

then T_t is a one-parameter completely positive semigroup with generator L given by

$$L(X) = -i[H_S, X] + \lambda^2(G^\dagger XG - \frac{1}{2}[G^\dagger G, X]_+) + \mu^2(GXG^\dagger - \frac{1}{2}[GG^\dagger, X]_+). \quad (12)$$

Thus U plays the role of a unitary quantum stochastic dilation of the quantum dynamical semigroup T_t with generator L given by (12) (see Gorrini *et al* 1976).

When in the special case $\varepsilon = \eta = 1$, $G = i(a + a^\dagger) = iq$ and (11) reduces to

$$dU = U[-iq dQ - \{iH_S + \frac{1}{2}(\lambda_0^2 + \mu_0^2) q^2\} dt],$$

which with the initial value $U(0) = I$ can be explicitly solved as

$$U(t) = \exp(-iH_S t) \exp[-iq Q(t)]. \quad (13)$$

Here $Q(t)$ is a classical Gaussian process with covariance $\exp[Q(s)Q(t)] = (\lambda_0^2 + \mu_0^2) \min(s, t)$. In the limit $\beta \rightarrow \infty$ (zero temperature) $\mu_0^2 \rightarrow 0$ and $\lambda_0^2 \rightarrow 1$ and in this limit $Q(t)$ reduces to the standard Brownian process.

One can instead compute the evolved state $\rho_S(t)$ defined as:

$$\text{tr } \rho_S(t) X = \text{tr } \rho_S T_t(X)$$

and find that

$$\rho_S(t) = \rho_S - \varepsilon^2 / [\sigma^2(\varepsilon^2 + \eta^2)] \{1 - \exp[-t\sigma^2(\varepsilon^2 + \eta^2)]\} (aa^\dagger - a^\dagger a),$$

where $\sigma^2 = \lambda_0^2 + \mu_0^2 \geq 1$. Thus $\rho_S(t) = \rho_S$ for all t if and only if $\varepsilon = 0$. One can also show that $\varepsilon = 0$ is the condition needed for satisfying the detailed balance condition, and this case is known in the literature as the rotating wave approximation.

In general, $\rho_S(\infty) = \rho_S - \varepsilon^2 / [\sigma^2(\varepsilon^2 + \eta^2)] (aa^\dagger - a^\dagger a)$ and in the classical case of $\varepsilon = \eta = 1$, $\rho_S(t) = \rho_S - (2\sigma^2)^{-1} [1 - \exp(-2t\sigma^2)] (aa^\dagger - a^\dagger a)$. The relaxed state at large time is thus different from the initial state.

4. Non-uniqueness of dilations of dynamical semigroups

Here we look at a specific example of a dynamical semigroup, constructed from a model as in Dattagupta (1984). The system observables $XB(h_S)$ in this model evolve under a dynamical semigroup T_t with generator L given by

$$L(X) = -i[H_S, X] + \lambda(WXW^* - X), \quad (14)$$

where H_S is the Hamiltonian of conservative Hiesenberg-type evolution, W is unitary in h_S , and $\lambda \geq 0$ is a parameter of the model.

The first kind of dilation $U^{(1)}$ is given in terms of the quantum Poisson process with intensity λ viz. $\pi_\lambda(t) = \Lambda(t) + \sqrt{\lambda}[A(t) + A^\dagger(t)] + \lambda t$. Here the gauge or

conservation process $\Lambda(t)$ is defined as in Hudson and Parthasarathy (1984). One can easily verify the Ito product rule: $(d\pi_\lambda)^2 = d\pi_\lambda$ and also that $\text{Exp } \pi_\lambda \equiv \langle \Omega, \pi_\lambda \Omega \rangle = \lambda t$. We write down the quantum stochastic differential equation (q.s.d.e) satisfied by $U^{(1)}(t)$ as

$$dU^{(1)} = U^{(1)} [(W-1) d\pi_\lambda - iH_S dt], \quad U^{(1)}(0) = I. \quad (15)$$

One can easily solve such an equation. However, it is more interesting to verify that such an $U^{(1)}$ is indeed a dilation of T_t given by (14)

The second kind of dilation $U^{(2)}$ is given entirely in terms of quantum Brownian motion. Here we write

$$dU^{(2)} = U^{(2)} \left[\sqrt{\lambda} W dA - \sqrt{\lambda} W^* dA^\dagger - \left(iH_S + \frac{\lambda}{2} \right) dt \right], \quad U^{(2)}(0) = I. \quad (16)$$

Again one can verify that the semigroup computed as $T_t(X) = \langle \cdot \otimes \Omega, U^{(2)} X U^{(2)*} \cdot \otimes \Omega \rangle$ has as generator L with the form given by (14). Thus we see that the same physical semigroup of evolution given by (14) has two dilations, one given entirely in terms of the quantum Poisson process and the other in terms of the quantum Brownian motion only.

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On the use of generalized Euler transformation in handling divergent series

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Abstract. A parametrized version of the Euler transformation, introduced fairly recently, is employed to study the behaviour of functions, given their formal power-series (alternating) expansions in λ with finite radii of convergence, in the limit $\lambda \rightarrow \infty$. The strategy requires only the first few low-order data. Results are tested with quite a few known cases and found remarkably satisfactory. The role of some other methods in this context are briefly discussed.

Keywords. Power series; divergence; perturbation theory; asymptotic expansions; Euler transformation.

1. Introduction

The appearance of divergent series is quite common in various fields of theoretical physics and chemistry (see, for example, Baker 1965; Baker and Gammel 1970) and these days one would *not* agree with Abel's remark (Hardy 1956) that 'it is shameful to base on them any demonstration whatsoever'.

A series representation of some function $F(\lambda)$ of the form

$$F(\lambda) = \sum_i f_i \lambda^i, \quad (1)$$

well outside the radius of convergence (λ_0), is only a formal one. However, in some cases, the asymptotic sum $F_a(\lambda) \approx F(\lambda)$ may be useful for small positive values of $(|\lambda| - \lambda_0)$. But, when $|\lambda| \gg \lambda_0$, $F_a(\lambda)$ makes no sense and we are really in trouble if $F(\lambda)$ is to be evaluated even to a moderate degree of accuracy. To deal with such cases, fortunately, a number of strategies are now available (and are being developed) which offer reliable estimates of $F(\lambda)$, given the coefficients f_i . Of these, the more widely studied ones during the past few years are the Padé approximants (PA) (Baker 1965, 1975; Baker and Gammel 1970; Baker and Graves-Morris 1980), the Borel transformation (Hardy 1956; Zinn Justin 1981; Simon 1982), continued fraction techniques (CFT) (Wall 1948; Jones and Thron 1980; Cizek and Vrscay 1982, 1984; Vrscay 1986), Aitken's Δ^2 method (Baker and Graves-Morris 1980), Wynn's ϵ -convergence algorithm (Shanks 1955), the method of order-dependent mapping (ODM) (Seznec and Zinn Justin 1979), the functional method (Arteca *et al* 1984) etc.

Most of the above techniques employ a considerably large number of coefficients f_i to obtain $F(\lambda)$ rather accurately. However, often, it so happens that one does not

have accurate estimates of f_i in hand except for the very first few, due chiefly to the complicated nature of the problem concerned. Keeping this *practical* difficulty in mind, we have recently developed (Bhattacharyya 1982) a parametrized version of the well-known Euler transformation, to be henceforth called the parametrized Euler transformation (PET). It has been observed that such simple 1- and 2-parameter transforms work very successfully, keeping in mind our limitations regarding the knowledge of $\{f_i\}$. For further applications and employment of some variants of this transformation, we refer to Silverman (1983) and Sangaranarayanan and Rangarajan (1983, 1984). The PET, we have explicitly demonstrated, is closely related to PA, and hence to CFT of specific varieties. Sangaranarayanan and Rangarajan (1983) found a close kinship of PET(1), the 1-parameter transform, to Aitken's Δ^2 method. Thus, PET appears to be a very general scheme by which a poorly-converging series may be accelerated or, more profitably, a divergent series can be successfully handled.

Perturbation theory often offers itself as a logical candidate for applying the various techniques of handling divergent series, not just because accurate results of $F(\lambda)$ are otherwise available, the coefficients f_i are known to considerably large orders, or because of practical importance; the more interesting aspect is that there are some inherent flexibilities in a perturbative approach which *can* be employed for series-acceleration. Stated otherwise, perturbation theory by itself is capable of offering some specific summability schemes. These are actually achieved by scaling. Rather surprisingly, one finds that such *basically perturbative* summability techniques are also versions of the PET (for detail, see Bhattacharyya 1982). This observation again points to the increased generality of the PET. In other cases, however, one has to check whether a particular technique is *superior* to these scaling schemes. Only, PA of specific types have correspondences with scaling of the zero-order Hamiltonian (Wilson *et al* 1977).

The primary aim of the present communication is to explore whether, by employing the PET, some information about the behaviour of $F(\lambda)$ in the limit $\lambda \rightarrow \infty$ can be extracted, if the parent series (1) of $F(\lambda)$ is known to, say, the third order, i.e. the coefficients from f_4 onwards are all unknown. At a first thought, it appears ridiculous. If at all, the sum

$$F(3) = \sum_{i=0}^3 f_i \lambda^i \quad (2)$$

can at best approximate $F(\lambda)$ only when $\lambda \rightarrow 0$, $\lambda_0 > 0$. On the other hand, if $\lambda_0 = 0$, $f(3)$ may satisfy $f(3) \approx F_a(\lambda) \approx F(\lambda)$, again for very small values of $|\lambda|$ and over a small range. But, as we shall see, the coefficients f_i indeed contain reasonable information regarding the large- λ behaviour of $F(\lambda)$. However, there is a condition: the series expansion (1) *must be alternating* in nature. Of course, this is a severe restriction and has to be ensured a priori. Also, it limits the applicability of the scheme we are going to propose. Still, we may remark that there are many such alternating series where some kind of symmetry forces them to be so. It is precisely in these cases where without explicitly calculating the higher-order coefficients ($\geq f_4$) we can be certain about the signs of such terms. Anyway, the problem that we have posed here is in no way going to become a trivial one owing to the imposed alternating nature of $F(\lambda)$. Moreover, to our knowledge, *none* of the summability schemes have ever been employed for this purpose with such little resource. Thus,

the PET will probably be the first scheme to play a significant role in this context. We shall also pay some attention to building up a connection between the PET and the generalized Euler transformation (GET) of Silverman (1983). A link between the ODM and the PET (2) will again be considered very briefly. Finally, the possibility of profitably using some of the other summability techniques with the information we extract will be indicated.

Our organization will be as follows. In §2, some aspects of the PET will be considered, for convenience. Section 3 will deal with the workability of the scheme. An introduction to the possible use of some other techniques in this particular context will be taken up in §4. We reserve §5 for a discussion on the relation of the PET with GET and ODM. In §6, some problems regarding the workability of the present scheme will be discussed.

2. Aspects of the PET

The Euler transformation (Morse and Feshbach 1953) is basically concerned with a change of variable. Thus, for an alternating series of the form

$$\bar{F}(\lambda) = \sum_{i=0} (-1)^i f_i \lambda^i, \quad (3)$$

a new variable $\lambda_1 = \lambda/(1+\lambda)$ is chosen to obtain

$$\bar{F}(\lambda) = [1/(1+\lambda)] \sum_{i=0} f_i^{(1)} \lambda_1^i, \quad (4)$$

where the new coefficients are related to the old ones. For non-alternating series of the form (1), it is sometimes useful to define a new variable, $\bar{\lambda}_1 = \lambda/(1-\lambda)$, to find

$$F(\lambda) = [1/(1-\lambda)] \sum_{i=0} \bar{f}_i^{(1)} \bar{\lambda}_1^i. \quad (5)$$

In the above cases, we actually applied the transformation repeatedly. But, we could have applied it a finite number of times. For example, if we apply it just once to (3), we obtain

$$\bar{F}(\lambda) = [f_0/(1+\lambda)] + \lambda_1 \sum_{i=0} (-1)^n (f_n - f_{n-1}) \lambda^n. \quad (6)$$

The GET (Morse and Feshbach 1953) involves a known function $G(\lambda)$ of the form

$$G(\lambda) = \sum_{i=0} g_i \lambda^i, \quad (7)$$

and leads, for the series (1), to the transformed expansion

$$F(\lambda) = \sum_{i=0} (-1)^i D_i \frac{\lambda^i}{i!} \frac{d^i}{d\lambda^i} G(\lambda), \quad (8)$$

$$\text{where } D_i = \sum_{r=0}^i (-1)^r \binom{i}{r} a_r, \quad a_r = f_r/g_r. \quad (9)$$

For the series (3), we have taken $G(\lambda) = (1+\lambda)^{-1}$.

As regards the PET, we have considered the 1- and 2-parameter transforms—PET(1) and PET(2), respectively. In PET(1), we have taken $G(\lambda) = (1 + k\lambda)^{-1}$ and in PET(2), the auxiliary function has been rendered more flexible by choosing it as $(1 + k\lambda)^{-m}$, where k and m are two adjustable parameters. Such transformations may again be applied just once or repeatedly. The new variables in the latter case become $\lambda/(1 + k\lambda)$ and $\lambda/(1 + k\lambda)^m$, respectively, for PET(1) and PET(2). For a detailed discussion and explicit relations, we refer to the original work (Bhattacharyya 1982).

Here we shall mainly concentrate on PET(2) and apply it just once to a series like (1) to obtain

$$F(\lambda) = [1/(1 + k\lambda)^m] \left(f_0 + \lambda \sum_{i=0}^{\infty} D_1 f_i \lambda^i \right), \quad (10)$$

$$\text{where } D_1 f_{n-1} = \sum_{r=0}^n f_{n-r} \binom{m}{r} k^r. \quad (11)$$

The parameters k and m are fixed by setting

$$D_1 f_0 = 0 = D_1 f_1, \quad (12)$$

to approximate $F(\lambda)$ by

$$F(\lambda) \approx f_0 (1 + k\lambda)^{-m}, \quad (13)$$

where

$$k = (f_1^2 - 2f_0 f_2)/f_0 f_1, \quad m = f_1^2/(2f_0 f_2 - f_1^2). \quad (14)$$

This is termed as the $[0, 2]$ PET(2), i.e. the right side of (13) is designated by $[0, 2]$ PET(2) $F(\lambda)$. If, on the other hand, we split $f(\lambda)$ as

$$f(\lambda) = f_0 + \lambda \sum_{i=1}^{\infty} f_i \lambda^{i-1} = f_0 + \lambda F_1(\lambda), \quad (15)$$

and construct $[0, 2]$ PET(2) $F_1(\lambda)$ along similar lines, we obtain another approximation for $F(\lambda)$ which we shall denote by

$$F(\lambda) \approx f_0 + \lambda [0, 2] \text{ PET(2) } F_1(\lambda) = [1, 3] \text{ PET(2) } F(\lambda). \quad (16)$$

For alternating series, the *most* important point that we like to mention here is that either the following inequality,

$$[0, 2] \text{ PET(2) } F(\lambda) > F(\lambda) > [1, 3] \text{ PET(2) } F(\lambda), \quad (17)$$

is obeyed or the reverse,

$$[0, 2] \text{ PET(2) } F(\lambda) < F(\lambda) < [1, 3] \text{ PET(2) } F(\lambda), \quad (18)$$

holds. We are yet to prove these inequalities, but many cases have been studied and the inequalities, either (17) or (18), are found to be satisfied. In fact, we have noticed that any two successive PET(2) obey either of them. This is an additional qualification of the PET.

3. Applications

Before proceeding further, a brief outline of the scheme that we shall follow deserves mention. So, we first discuss what exactly is to be done and what information is needed.

3.1 The scheme

Choose an alternating series for which f_0 to f_3 are known. Be sure that λ_0 is finite. Find from some other source one or two values of $F(\lambda)$, reasonably accurate, when $|\lambda| \gg \lambda_0$. Check the inequalities (17) or (18) after constructing the $[0, 2]$ and $[1, 3]$ PET(2) approximants to $F(\lambda)$ in regions $|\lambda| \gg \lambda_0$. Choose now the closer approximant and infer from its behaviour how $F(\lambda)$ will change with λ in the limit $\lambda \rightarrow \infty$. The variation of $F(\lambda)$ with λ in this limit will thus be bounded either above or below by virtue of (17) or (18).

We may remark at this stage that (i) if values of $F(\lambda)$, $|\lambda| \gg \lambda_0$ are not available, one still obtains bounds to variations of $F(\lambda)$ with λ , for large λ , but one of such bounds may not be very useful; (ii) such a procedure is of value if λ_0 is finite; (iii) it is unlikely that at two different λ -values beyond λ_0 , two *different* said approximants are closer. Regarding the last point, our experience is that if, e.g., the $[0, 2]$ PET(2) approximant is closer to $F(\lambda)$ for some $|\lambda| > \lambda_0$, it *continues* to remain so. Moreover, it does not change its role—if it is found to be an upper bound for some $|\lambda| > \lambda_0$, the property continues.

3.2 Some examples

$$(i) \quad \ln(1+\lambda) = \lambda(1 - \lambda/2 + \lambda^2/3 - \lambda^3/4 + \dots) \quad (19)$$

Here, for large λ , one finds the $[0, 2]$ variety closer and that

$$F(\lambda) < [0, 2] \text{ PET}(2) F(\lambda) = \lambda/(1 + \frac{5}{6}\lambda)^{3/5}. \quad (20)$$

Thus, we have

$$F(\lambda) < \sim \lambda^{2/5}, \quad (21)$$

which cannot be directly tested, however. Another interesting feature emerges from (20). We find

$$1 + \lambda \leq e^{\lambda/(1+5\lambda/6)^{3/5}}, \quad (22)$$

$$\text{or,} \quad e \geq (1 + \lambda)^{(1+5\lambda/6)^{3/5}/\lambda}, \quad (23)$$

which holds for any λ . Writing $\lambda = 1/n$ we obtain

$$e \geq \left(1 + \frac{1}{n}\right)^{n(1+5/6n)^{3/5}}, \quad (24)$$

which may be compared with the standard definition of e

$$e = \lim_{n \rightarrow \infty} \left(1 + \frac{1}{n}\right)^n, \quad (25)$$

ignoring the limit or, with a recently introduced (Mermin 1984) refined variety[†],

$$e \approx \left(1 + \frac{1}{n}\right)^{n+\frac{1}{2}}. \quad (26)$$

Table 1 shows the results. The bounding nature of (25), $e \geq (1+1/n)^n$, follows from the inequality $\ln(1+\lambda) \leq \lambda$ for $0 \leq \lambda$. On the other hand, (26) offers no such systematism. The advantage of using PET(2) is clear from the table.

$$(ii) \quad \frac{\tan^{-1} \lambda}{\lambda} = 1 - \lambda^2/3 + \lambda^4/5 - \dots \quad (27)$$

In this case, one finds that again the $[0, 2]$ approximant is closer to the function for large λ . Calculation shows

$$\lim_{\lambda \rightarrow \infty} \frac{\tan^{-1} \lambda}{\lambda} < \sim \lambda^{-10/13}. \quad (28)$$

The agreement is remarkable if we remember that $\lim_{\lambda \rightarrow \infty} \tan^{-1} \lambda = \pi/2$ and hence the left part of (28) varies as λ^{-1} .

(iii) We shall now consider the anharmonic oscillator case for which the Hamiltonian is

$$H = -\nabla^2 + x^2 + \lambda x^4. \quad (29)$$

The energy eigenvalues $E_n(\lambda)$ for such a system are known to be *formally* represented by alternating power-series expansions in λ . The expansion coefficients are taken from Reid (1967). We have studied this system earlier and found that the $[0, 2]$ PET(2) is closer to $E_n(\lambda)$ for any λ and n (note that here $\lambda_0 = 0$) and obeys

$$E_n(\lambda) > [0, 2] \text{ PET}(2) E_n(\lambda). \quad (30)$$

An important point with such eigenvalue functions is that the large- λ behaviour of every $E_n(\lambda)$ is the same: $\lim_{\lambda \rightarrow \infty} E_n(\lambda) \sim \lambda^{1/3}$. This, in fact, follows from a

coordinate scaling argument applied to H and is originally due to K Symanzik (Simon 1970). The results are presented in table 2. Clearly, the approximate behaviour gradually improves with n , though it is unlikely to reach the exact value. After all, that is too much to expect from such a simple scheme involving really *very limited* information.

Table 1. The value of e .

n	$(1+1/n)^n$	$(1+1/n)^{n+1/2}$	$(1+1/n)^{n(1+5/6n)^{3/5}}$
1	2.0	2.828...	2.7106...
10	2.59...	2.7203...	2.71826...
100	2.704...	2.71830...	2.718281....

[†]It follows from (24) as a first approximation to modify (25) for finite n .

Table 2. Large- λ behaviour of eigenvalues of H given by (29).

$n =$	0	1	2	3	5	7	10	20
$E_n(\lambda) >$	$\lambda^{0.1765}$	$\lambda^{0.1852}$	$\lambda^{0.1983}$	$\lambda^{0.2033}$	$\lambda^{0.2067}$	$\lambda^{0.2079}$	$\lambda^{0.2086}$	$\lambda^{0.2091}$

(iv) Here we choose the hydrogenic s -state Hamiltonian perturbed by a radial electric field

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r} + \lambda r, \quad (31)$$

and consider the ground state eigenvalue $E_0(\lambda)$ for which the expansion coefficients are available (Austin 1980). A scaling argument in this case dictates that the eigenvalues $E_n(\lambda)$ should behave as $\sim \lambda^{2/3}$ in the large- λ regime. For this system, calculation shows that the $[1, 3]$ approximant is closer to $E_0(\lambda)$, $\lambda > \lambda_0 = 0$, and obeys

$$E_0(\lambda) < [1, 3] \text{ PET}(2) E_0(\lambda). \quad (32)$$

Also,

$$\lim_{\lambda \rightarrow \infty} [1, 3] \text{ PET}(2) E_0(\lambda) \sim \lambda^{0.875}, \quad (33)$$

so that we get the result

$$\lim_{\lambda \rightarrow \infty} E_0(\lambda) < \sim \lambda^{0.875}. \quad (34)$$

Needless to mention, we could have also taken advantage of other n -values to obtain, hopefully, still better estimates.

(v) As the last example, we take the function

$$\int_0^\infty e^{-t} dt / (1 + \lambda t) = 1 - 1! \lambda + 2! \lambda^2 - 3! \lambda^3 + \dots, \quad (35)$$

with the associated expansion ($\lambda_0 = 0$) which is again asymptotic in nature. The value of the function at $\lambda = 1$ is ≈ 0.5963 and it may be checked that the $[0, 2]$ PET(2) approximant is closer to this value satisfying

$$F(\lambda) < [0, 2] \text{ PET}(2) F(\lambda). \quad (36)$$

Further, the right side of (36) in the large- λ limit becomes $\sim \lambda^{-1/3}$ so that we have

$$\lim_{\lambda \rightarrow \infty} F(\lambda) < \sim \lambda^{-1/3}. \quad (37)$$

Actually, however, $\lim_{\lambda \rightarrow \infty} F(\lambda) \sim (\ln \lambda)/\lambda$. The result (37) that we have just

obtained here is not very good if we remember the result of our first example $\ln(\lambda+1) \approx \ln \lambda < \sim \lambda^{2/5} (\lambda \rightarrow \infty)$. Coupling this with the exact behaviour we find

$$\lim_{\lambda \rightarrow \infty} F(\lambda) \sim \frac{\ln \lambda}{\lambda} < \lambda^{-0.6}, \quad (38)$$

which immediately points to the rather poor performance of (37).

3.3 Discussion

Our observations are collected in table 3. It demonstrates convincingly the power of the PET in extracting the behaviour of $\lim_{\lambda \rightarrow \infty} F(\lambda)$ from just the first few terms. $E(\lambda)$ in this table refers to any eigenvalue of the Hamiltonian defined by (29) and $E_0(\lambda)$ signifies the ground state eigenenergy corresponding to the Hamiltonian (31). Let us note that the worst estimate is obtained for (35). Indeed, the goodness of the predicted behaviour depends on the *tightness* of the bounds. In certain situations, to avoid looseness of the bounds, we are free to take the derivative series. The point is, one should then have at least one or two accurate data for the derivative for λ -values well beyond λ_0 .

4. Role of a few other techniques

As we have mentioned earlier, so far no summability technique has been used for the purpose in hand. But it is easy to see that if the large- λ behaviour of $F(\lambda)$

Table 3. Large- λ behaviour of some functions.

$F(\lambda)$	$\lim_{\lambda \rightarrow \infty} F(\lambda)$	
	Predicted	Exact
$\ln(1+\lambda)$	$< \lambda^{0.4}$	—
$\frac{\tan^{-1} \lambda}{\lambda}$	$< \lambda^{-0.77}$	λ^{-1}
$E(\lambda)$	$> \lambda^{0.209}$	$\lambda^{0.333}$
$E_0(\lambda)$	$< \lambda^{0.875}$	$\lambda^{0.667}$
$\int_0^\infty \frac{e^{-t} dt}{1+\lambda t}$	$< \lambda^{-0.33}$	$\frac{\ln \lambda}{\lambda} < \lambda^{-0.6}$

is known beforehand, we can profitably employ suitable summability schemes. For example, if $\lim_{\lambda \rightarrow \infty} F(\lambda) \sim \lambda^m (m : \text{integer})$ we may advocate the use of $[(n+m)/n]$ PA ($n = 0, 1, 2, \dots$) for $m > 0$. Similarly, if m were a negative integer, $[n/(n+m)]$ PA could be tried at first. On the other hand, if $\lim_{\lambda \rightarrow \infty} F(\lambda) \sim \text{constant}$, we can try $[n/n]$ PA. Keeping in mind the close

correspondence between the PA and the CFT, we refrain from a discussion on the possible impact of a knowledge of $F(\lambda)$ (in the large- λ regime) on CFT. Rather, we note that such information is efficiently taken into account in schemes like the ODM or the functional method, leading thus to very accurate estimates of $f(\lambda)$ for $|\lambda| \gg \lambda_0$.

It is now quite apparent that, in the aforesaid issue, potential use of the information we obtain by employing the PET (2) can be made. Thus, our results will *at least* help us in selecting certain other summability techniques to be employed for accurate data. Such a selection is likely to be advantageous, though not always; at least we can say that it will *not* be disadvantageous as compared to some *randomly* selected scheme. For example, Leinaas and Osnes (1980) used $[(n+1)/n]$ PA and coupled Borel-Pade approximants on their way to studying a model intruder problem, guided by the linear λ -dependence of $E(\lambda)$ for large $|\lambda|$ and found encouraging results for negative values of λ . For positive λ , however, the results were not found to be *quite* satisfactory. Likewise, Baker (1965) discussed a few cases where $[n/n]$ PA show an *oscillatory* behaviour, though the functions concerned obey $\lim_{\lambda \rightarrow \infty} F(\lambda) \sim \text{constant}$. Keeping aside such pathological cases, we may hope that the predicted large- λ behaviour will guide us properly towards betterment.

5. The PET, GET and ODM

The GET put forward by Silverman (1983) rests on a change of variable from λ to μ , where

$$\mu = \lambda/(1 - \sigma\lambda), \quad (39)$$

and the parent series $F(\lambda)$ is rewritten as

$$F(\lambda) = \left(\frac{1}{1 - \sigma\lambda} \right)^m \sum_{j=0}^m a_j \mu^j, \quad a_j = a_j(\sigma, m). \quad (40)$$

Another transformation that has been used corresponds to just a scaling of the new variable μ :

$$\nu = (1 - \sigma)\mu, \quad (41)$$

and this need not be considered for the present purpose. We note first that this is actually a two-parameter transform. But, whereas in our case the variable was of the form (if applied repeatedly),

$$\lambda_{km} = \lambda / (1 + k\lambda)^m, \quad (42)$$

here the variable μ is of the same form as our PET(1) case. In other words, the transformation leading to (40) is actually a *mixed* transformation, as we have checked. First, the PET(2) is applied *just once* by choosing $(1 - \sigma\lambda)^{m-1}$ as the parametrized function and then, to the new series that has emerged, the PET(1) is applied *repeatedly* by choosing $(1 - \sigma\lambda)$ as the parametrized function [see (21)–(24) in Bhattacharyya 1982]. We fail to recognize how ‘in several fundamental aspects’ this particular GET differs from earlier work, though the author claims that it is so.

Repeated application of the PET(2) leads ultimately to

$$F(\lambda) = [1/(1 + k\lambda)^m] \sum_{i=0} D_i f_0 \lambda_{km}^i, \quad (43)$$

where λ_{km} is given by (42), and

$$D_p f_{n-1} = \sum_{r=0}^n D_{p-1} f_{n-r} \binom{m}{r} k^r. \quad (44)$$

Rewriting (43) as

$$F(\lambda) (1 + k\lambda)^m = \sum_{i=0} b_i \lambda_{km}^i, \quad (45)$$

and viewing the left hand side as some series in λ , we may say that the PET(2) has actually transformed some $\sum_i c_i \lambda^i$ to $\sum_i b_i \lambda_{km}^i$. Here $\{c_i\}$ and $\{b_i\}$ are naturally related through k and m . Let us now go back from $\sum_i b_i \lambda_{km}^i$ to $\sum_i c_i \lambda^i$. This will be achieved by putting the relation (42) in the former series for some chosen k and m . If, instead, we like to go back to a scaled- λ series, (42) is to be accordingly modified and then employed in $\sum_i b_i \lambda_{km}^i$. This modified version of (42) will read as

$$\lambda_{km} = \alpha\lambda / (1 + k\alpha\lambda)^m. \quad (46)$$

Choosing $k = \alpha^{-1}$, the method of ODM follows immediately. Thus, we recognize ODM as the *scaled inverse* of the PET(2). This completes our discussion on the relationship of the PET(2) with the GET and the ODM.

6. Some unsolved problems

The first problem that we wish to mention is concerned with the bracketing nature of the two consecutive $[p, p+2]$ PET(2) approximants. We have found that this is obeyed for alternating series by choosing a variety of examples. But, a rigorous proof is necessary.

Secondly, we remark that here we are working with power-series expansions for which our scheme leads to either $F(\lambda) \sim \lambda^\alpha$ - or $F(\lambda) \sim \lambda^{-\alpha}$ -type of behaviour (α : some positive number) as $\lambda \rightarrow \infty$. Hence, functions which either have some kind of exponential dependencies*, or obey $\lim_{\lambda \rightarrow \infty} F(\lambda) \sim \text{constant}$

(finite, nonzero), are unlikely to conform to our scheme. We should, in such unknown situations, be prepared for a poor performance of the PET. Indeed, this is why we have chosen the function $\tan^{-1} \lambda/\lambda$, instead of just $\tan^{-1} \lambda$, as one of the examples. Suitable ways of tackling such situations are wanted.

The third problem is to enquire if there exists a *systematic* way to improve our results. We are not sure whether 3- or 4-parameter transforms, or still higher ones, will also bracket functions defined formally by alternating power-series expansions with increasing tightness. But some such scheme should be constructed.

7. Conclusions

Our endeavour has been to obtain information about the large- λ behaviour of functions for which formal power-series expansions are supplied to a very low order, provided that such expansions are alternating in nature. For convenience, one or two values of the functions well beyond λ_0 , the actual radii of convergence, are to be supplied. With such limited resource, we have found that reasonably approximate behaviour *can* be predicted.

It may be argued that mathematical rigour has been relegated to second place throughout. This is true and we may emphasize here that work on divergent series handling techniques *are mostly* empirical in nature. Moreover, if the available resource is very limited, as we require here, one probably cannot be rigorous at the same time. This is precisely why we have stressed on the simplicity of this scheme.

Finally, we have summarized a few unsolved problems. We hope that solutions to such problems will decide the status of PET in the near future.

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*This case may be tackled indirectly by employing the $\ln F(\lambda)$ -series.

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Note added in proof

Prof. S. K. Rangarajan has recently noted (private communication) that

$$[0/1]PA(d \ln F(\lambda)/d\lambda) = d \ln ([0, 2] \text{ PET}(2) F(\lambda))/d\lambda.$$

This identity, once again, points to the increased generality of the PET. As $F(\lambda) \sim \lambda^\alpha$ (α : any real number) for large λ , one must take the $d \ln F(\lambda)/d\lambda$ series to construct the *natural* $[n/n+1]$ PA. The identity nicely involves the *first* members of both the said PA and the PET. More about the importance of such a relation will be discussed elsewhere. The author is thankful to Prof. Rangarajan for his interest in the work and to INSA for partial financial support.

Quantum chemistry in phase space: Some current trends

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Abstract. Recent developments in the phase space formalisms within density functional theory are discussed. The phase space distribution function corresponding to a ground state electron density, obtained through an entropy maximization procedure, leads to good quality momentum density and first order reduced density matrix. Calculations of Compton profiles and exchange energies with different kinetic energy functionals show interesting results.

Keywords. Density functional theory; phase space distribution function; momentum density; Compton profile; exchange energy; information theory; local thermodynamics.

1. Introduction

Quantum mechanical description of a many-electron system is usually based on the configuration space wavefunction $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ or the electron density $\rho(\mathbf{r})$ (Bamzai and Deb 1981; Ghosh and Deb 1982; Parr 1983; March and Deb 1987) and only occasionally on the momentum space wavefunction $\chi(\mathbf{p}_1, \dots, \mathbf{p}_N)$ or the momentum density $\gamma(\mathbf{p})$ (Epstein 1973). Although either of the two spaces can provide the framework for a complete description, there has been an increasing interest recently in the phase space (PS) representation (Hillery *et al* 1984) of quantum mechanics. Apart from the redundancy, the PS language has been questioned also for apparent contradictions with the quantum mechanical uncertainty principle. These objections have however mostly been resolved and the PS approach has been highly useful in many applications viz photodissociation (Brown and Heller 1981), collisions (Carruthers and Zachariasen 1983), intra-molecular energy transfer (Hutchinson and Wyatt 1980) etc.

The PS distribution function was first introduced in quantum mechanics by Wigner (1932) and subsequently generalized by Moyal (1949) and others (see Hillery *et al* 1984 for a review). Wigner's PS function in reduced space is merely a particular representation of the reduced density matrix but, has the additional advantage of being able to provide a classical-like appearance to the formalism. This makes the nature of the quantum corrections transparent and thus the PS approach has a unique strength for semiclassical applications (Heller 1976).

Being a direct product of the position space and the momentum space, the phase space can also establish a bridge between these two spaces. The wavefunctions $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ and $\chi(\mathbf{p}_1, \dots, \mathbf{p}_N)$ are related simply by a Dirac-Fourier transform but the exact relationship between the two single-particle densities $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ is still unknown. Using the six-dimensional PS distribution function $f(\mathbf{r}, \mathbf{p})$ as an intermediate quantity, approximate but accurate transformations between the electron density and the momentum density (Parr *et al* 1986) have however been

suggested. In this paper, we discuss the current status of these prescriptions for interconnecting $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$. The resulting $f(\mathbf{r}, \mathbf{p})$ is also shown to lead to a good approximation to the first-order density matrix $\rho_1(\mathbf{r}; \mathbf{r}')$ and hence the exchange energy functional (Ghosh and Parr 1986) of the density functional theory (DFT) (Kohn and Sham 1965; Ghosh and Deb 1982; Parr 1983).

2. Formalism

The Wigner distribution function for a single particle system is defined as

$$f(\mathbf{r}, \mathbf{p}) = (2\pi)^{-3} \int \psi^*(\mathbf{r} + \mathbf{s}/2) \psi(\mathbf{r} - \mathbf{s}/2) \exp[-i\mathbf{p} \cdot \mathbf{s}] d\mathbf{s}. \quad (1)$$

For an N -particle system, a six-dimensional $f(\mathbf{r}, \mathbf{p})$ can be defined in terms of the first-order reduced density matrix $\rho_1(\mathbf{r}; \mathbf{r}')$, viz,

$$f(\mathbf{r}, \mathbf{p}) = (2\pi)^{-3} \int \rho_1(\mathbf{r} + \mathbf{s}/2; \mathbf{r} - \mathbf{s}/2) \exp[-i\mathbf{p} \cdot \mathbf{s}] d\mathbf{s}. \quad (2)$$

A reverse transform of (2) yields the density matrix $\rho_1(\mathbf{r}; \mathbf{r}')$ from $f(\mathbf{r}, \mathbf{p})$. The function $f(\mathbf{r}, \mathbf{p})$ also satisfies the marginal conditions:

$$\int f(\mathbf{r}, \mathbf{p}) d\mathbf{p} = \rho(\mathbf{r}), \quad (3a)$$

$$\int f(\mathbf{r}, \mathbf{p}) d\mathbf{r} = \gamma(\mathbf{p}). \quad (3b)$$

The definition of a PS function is however not unique and a class of PS functions satisfying the marginals (3) is possible (Cohen 1966). Equation (3) however suggests that the construction of an appropriate $f(\mathbf{r}, \mathbf{p})$ from $\rho(\mathbf{r})$ should provide a route for generating $\gamma(\mathbf{p})$ from $\rho(\mathbf{r})$.

The simplest $f(\mathbf{r}, \mathbf{p})$ constructed from $\rho(\mathbf{r})$ corresponds to the Thomas Fermi (TF) approximation and is given by

$$f(\mathbf{r}, \mathbf{p}) = 2(2\pi)^{-3} \Theta[p_F^2(\mathbf{r}) - p^2], \quad (4)$$

where $p_F(\mathbf{r})$ is the Fermi momentum at position $\mathbf{r}$ and Θ is the Heaviside theta function. Integration over $\mathbf{p}$ leads to the well-known TF relation

$$\rho(\mathbf{r}) = (3\pi^2)^{-1} p_F^3(\mathbf{r}). \quad (5)$$

The expectation value $\langle p^n \rangle$ obtained from (4) is:

$$\begin{aligned} \int \int p^n f(\mathbf{r}, \mathbf{p}) d\mathbf{p} d\mathbf{r} &= (4\pi^3)^{-1} \int \int p^n \Theta[p_F^2(\mathbf{r}) - p^2] d\mathbf{p} d\mathbf{r} \\ &= [\pi^2(n+3)]^{-1} \int p_F^{n+3}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (6)$$

On using (3) and (5), (6) becomes

$$\int p^n \gamma(\mathbf{p}) d\mathbf{p} = [3/(n+3)] (3\pi^2)^{n/3} \int \rho^{(n+3)/3} d\mathbf{r}. \quad (7)$$

Equation (7) is the well-known Coulson and March (1950) relation interconnecting electron density and momentum density expectation values and has been extensively used by Gadre and Pathak (1981) and Pathak *et al* (1984) for calculations on atomic and molecular systems. It can however transform only a restricted class of density functionals in position space (of the form $\rho^{1+n/3}$) to those in momentum space.

A generalization can be obtained by evaluating the expectation value of an arbitrary function $g(p)$, viz,

$$\begin{aligned}\iint g(p)f(\mathbf{r}, \mathbf{p})d\mathbf{p}d\mathbf{r} &= (4\pi^3)^{-1} \iint g(p)\Theta[p_F^2(\mathbf{r}) - p^2]d\mathbf{p}d\mathbf{r} \\ &= (1/\pi^2) \int h[p_F(\mathbf{r})]d\mathbf{r},\end{aligned}\quad (8)$$

where

$$h(p_F) = \int g(p)p^2 d\mathbf{p}; \quad g(p) = (1/p^2)dh(p)/dp. \quad (9)$$

The generalized Coulson-March relationship is thus given by

$$\int g(p)\gamma(p)d\mathbf{p} = (1/\pi^2) \int h(p_F(\mathbf{r}))d\mathbf{r}, \quad (10)$$

and can be employed to transform any position space density functional to a momentum space one by first rewriting it as a function of $p_F(\mathbf{r})$ using $p_F(\mathbf{r}) = (3\pi^2\rho)^{1/3}$ and then using (9). Equation (10) has been recently obtained by Das and Ghosh (1987) and Das *et al* (1987) who have also used it to derive a correlation energy functional in momentum space.

An alternative information-theoretic approach to obtain an $f(\mathbf{r}, \mathbf{p})$ corresponding to the density $\rho(\mathbf{r})$ has recently been proposed in connection with a thermodynamic transcription of density functional theory (Ghosh *et al* 1984; Ghosh and Berkowitz 1985). Assuming the PS function to yield the correct density $\rho(\mathbf{r})$ and kinetic energy (KE) density $t(\mathbf{r}, \rho)$, viz,

$$\int f(\mathbf{r}, \mathbf{p})d\mathbf{p} = \rho(\mathbf{r}); \quad \int f(\mathbf{r}, \mathbf{p}) (p^2/2)d\mathbf{p} = t(\mathbf{r}, \rho), \quad (11)$$

the most appropriate distribution function is obtained through a maximization of the entropy functional defined as

$$S = -k \iint f[\ln f - 1]d\mathbf{p}d\mathbf{r}, \quad (12)$$

where k is the Boltzmann constant. The resulting PS function is given by

$$f(\mathbf{r}, p) = [\beta(\mathbf{r})/2\pi]^{3/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r})p^2/2], \quad (13)$$

where $\beta(\mathbf{r})$ is the Lagrange multiplier to the KE constraint and is given by $\beta(\mathbf{r}) = (3/2)\rho(\mathbf{r})/t(\mathbf{r}, \rho) = 1/kT(\mathbf{r})$. Here $T(\mathbf{r})$ is the local temperature defined in analogy with the ideal gas expression for KE, viz, $(3/2)\rho(\mathbf{r})kT(\mathbf{r}) = t(\mathbf{r}, \rho)$.

The spherically averaged momentum density $\gamma(p)$ and the Compton profile $J(q)$ are now given by (Parr *et al* 1986)

$$\gamma(p) = \int f(\mathbf{r}, \mathbf{p})d\mathbf{r} = \int d\mathbf{r} [\beta(\mathbf{r})/2\pi]^{3/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r})p^2/2], \quad (14)$$

and

$$\begin{aligned}J(q) &= (1/2) \int \gamma(p) (1/p)dp \\ &= (2\pi)^{-1/2} \int d\mathbf{r} \beta(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r})q^2/2].\end{aligned}\quad (15)$$

A reverse transform of (2) applied to $f(\mathbf{r}, p)$ of (13) yields the first-order density matrix

$$\rho_1(\mathbf{r} + \mathbf{s}/2; \mathbf{r} - \mathbf{s}/2) = \rho(\mathbf{r}) \exp[-s^2/2\beta(\mathbf{r})], \quad (16)$$

which leads to the exchange energy density functional

$$\begin{aligned}
 E_x[\rho] &= -(1/4) \int \int d\mathbf{r} d\mathbf{r}' |\mathbf{r} - \mathbf{r}'|^{-1} |\rho_1(\mathbf{r}; \mathbf{r}')|^2 \\
 &= -(\pi/2) \int \rho(\mathbf{r})^2 \beta(\mathbf{r}) d\mathbf{r}.
 \end{aligned} \tag{17}$$

Equations (14) and (15) form the basis for the prediction of the momentum space properties while (16) and (17) can be used to obtain the density matrix and the exchange energy from the electron density. The quantity $\beta(\mathbf{r})$ can be calculated from a suitable functional form for the kinetic energy density. Ghosh *et al* (1984), Parr *et al* (1986) and Ghosh and Parr (1986) made use of the orbital density form:

$$t(\mathbf{r}, \rho) = (1/8) \Sigma (\nabla \rho_i \cdot \nabla \rho_i) / \rho_i - (1/8) \nabla^2 \rho. \tag{18}$$

One can however employ the TF expression

$$t_0(\mathbf{r}, \rho) = (3/10) (3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3}, \tag{19}$$

or the gradient corrected result

$$t(\mathbf{r}, \rho) = t_0(\mathbf{r}, \rho) + (1/72) (\nabla \rho \cdot \nabla \rho) / \rho. \tag{20}$$

Although the Laplacian term of (18) does not contribute to the integrated result, it is however responsible for some interesting consequences (Yang 1986; Yang *et al* 1986). The coefficient (1/8) of the Laplacian has been shown to arise naturally from a density matrix expansion by Berkowitz (1986).

It is interesting to note that using $\beta(\mathbf{r})$ based on TF KE (19), one obtains from (17) the Dirac exchange formula with a factor (10/9). This leads to a value of $\alpha = (10/9) (2/3) = 0.74$ which is the mean of the α values for atoms viz 0.77 for He and 0.70 for Xe in X_α theory (Gopinathan *et al* 1976). Using (20) for calculating $\beta(\mathbf{r})$, one is led to a gradient correction for the exchange energy functional. Analogously, a connection with the Coulson-March formula (7) for the Compton profile can be established from (15) by using TF KE (19) for obtaining $\beta(\mathbf{r})$.

The TF based results can predict only spherically averaged momentum space properties. The PS function of (13) can however be generalized to enable prediction of anisotropy in momentum density (Parr *et al* 1986). Using the KE component densities $t_x(\mathbf{r}, \rho)$, $t_y(\mathbf{r}, \rho)$ and $t_z(\mathbf{r}, \rho)$ as constraints, the resulting PS function becomes

$$\begin{aligned}
 f(\mathbf{r}, \mathbf{p}) &= (2\pi)^{-3/2} [\beta_x(\mathbf{r}) \beta_y(\mathbf{r}) \beta_z(\mathbf{r})]^{1/2} \rho(\mathbf{r}) \\
 &\quad \exp[-(1/2) \{\beta_x p_x^2 + \beta_y p_y^2 + \beta_z p_z^2\}],
 \end{aligned} \tag{21}$$

where $\beta_x(\mathbf{r})$, $\beta_y(\mathbf{r})$ and $\beta_z(\mathbf{r})$ are the respective Lagrange multipliers for the three constraints. For a diatomic molecule, this leads to the expressions for the directional (parallel and perpendicular) Compton profiles:

$$J_{\parallel}(q) = (2\pi)^{-1/2} \int d\mathbf{r} \beta_{\parallel}(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta_{\parallel}(\mathbf{r}) q^2/2], \tag{22a}$$

$$J_{\perp}(q) = (2\pi)^{-1/2} \int d\mathbf{r} \beta_{\perp}(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta_{\perp}(\mathbf{r}) q^2/2]. \tag{22b}$$

The exchange energy functional of (17) however has been shown (Kemister 1986) to remain unchanged by this generalization and hence is applicable to atoms and molecules alike.

3. Results and discussion

The numerical results evaluated through (15) and (17) for the Compton profiles (Parr *et al* 1986) and the exchange energies respectively (Ghosh and Parr 1986) by using the Hartree-Fock density (Clementi and Roetti 1974) for noble gas atoms show good agreement with the actual ones. The directional Compton profiles from (22) also agree very well with the Hartree-Fock results for the N_2 molecule (Parr *et al* 1986).

In these calculations, the KE functional of (18) has been employed for obtaining $\beta(\mathbf{r})$. This is especially convenient when one does a Kohn and Sham (1965) type calculation which gives density through the orbital densities. The exchange potential corresponding to the exchange energy functional of (17) with $\beta(\mathbf{r})$ defined through (18) can then be directly incorporated in the self consistent scheme.

It is interesting to study the effect of using other approximate KE density functionals [e.g. (19) or (20)] for obtaining $\beta(\mathbf{r})$ in the calculations. Some illustrative numerical results of such calculations using (20) are presented for the Compton profiles and exchange energies respectively in tables 1 and 2 for the atoms

Table 1. Compton profiles $J(q)$ for atoms.

q	Ne					Ar				
	PRG ^a	PRGwL ^b	TFW ^c	TFWL ^d	HF ^e	PRG ^a	PRGwL ^b	TFW ^c	TFWL ^d	HF ^e
0.0	2.98	2.50	3.15	3.43	2.73	5.49	4.78	5.82	6.28	5.06
0.2	2.91	2.47	3.03	3.18	2.70	5.27	4.66	5.49	5.66	4.96
0.4	2.72	2.38	2.74	2.76	2.59	4.70	4.33	4.74	4.71	4.62
0.6	2.45	2.24	2.39	2.36	2.41	3.96	3.84	3.91	3.86	4.04
0.8	2.14	2.06	2.05	2.01	2.17	3.22	3.28	3.19	3.16	3.33
1.0	1.82	1.86	1.75	1.71	1.89	2.59	2.72	2.60	2.58	2.66
1.2	1.53	1.64	1.48	1.45	1.61	2.10	2.22	2.13	2.13	2.11
1.6	1.06	1.22	1.07	1.05	1.12	1.47	1.49	1.49	1.48	1.42
2.0	0.730	0.855	0.770	0.761	0.771	1.12	1.11	1.10	1.09	1.08
3.0	0.331	0.347	0.349	0.347	0.346	0.712	0.740	0.668	0.654	0.736
5.0	0.123	0.131	0.107	0.103	0.124	0.333	0.376	0.335	0.330	0.359
10.0	0.024	0.031	0.024	0.024	0.022	0.073	0.078	0.069	0.068	0.075

^a Equations (15) and (18) of text; results from Parr *et al* (1986); ^b equations (15) and (18) of text; but without the Laplacian term in the latter; ^c equations (15) and (20) of text; ^d equations (15) and (20) of text; but with an additional $(-1/72)\nabla^2\rho$ term in the latter; ^e results from Biggs *et al* (1975): numerical Hartree-Fock wavefunctions.

Table 2. Exchange energies for atoms.

Atoms	Exact ^a exchange	GP ^b exchange	GPwL ^c exchange	TFW ^d exchange	TFWL ^e exchange
Ne	12.11	11.57	12.81	11.23	11.51
Ar	30.18	29.24	31.70	28.86	29.51

^a Results from Perdew (1985); ^b equations (17) and (18) of text; results from Ghosh and Parr (1986); ^c equations (17) and (18) of text; but without the Laplacian term in the latter; ^d equations (17) and (20) of text; ^e equations (17) and (20) of text; but with an additional $(-1/72)\nabla^2\rho$ term in the latter.

Ne and Ar. Calculations have been made with and without the inclusion of the Laplacian term, which however makes the KE density nonunique. The results indicate that this term plays an important role in the present prescription. It may be noted that the coefficients of the Laplacian term are taken as (1/8) and (1/72) for (18) and (20) respectively to ensure positivity of the resulting KE density at least for atomic systems.

The numerical results on Compton profiles as well as the exchange energies for the approximate KE functional (20) seem to be less accurate. This is perhaps a consequence of the poor local behaviour of these functionals although they show good accuracy for the global KE values for atomic (Ghosh and Balbas 1985; Ghosh and Parr 1985) as well as molecular systems (Allan *et al* 1985; Deb and Chattaraj 1986; Lee and Ghosh 1986). Better KE functionals with proper local behaviour (Deb and Ghosh 1983; Chattaraj and Deb 1984; Ghosh and Balbas 1985; Ghosh and Parr 1985; Yang *et al* 1986) are however expected to yield better results.

4. Concluding remarks

The present paper discusses the PS approach from the point of view of its use as a calculational tool e.g. for establishing a bridge between the position space and momentum space. The PS function that has been obtained here through an entropy maximization (Levine and Tribus 1979) has recently been shown (Berkowitz 1986) to be a well-defined approximation to the Wigner distribution function. The present PS function also leads to a local thermodynamic transcription (Ghosh *et al* 1984) and a classical fluid-like approach (Ghosh and Berkowitz 1985) corresponding to the ground state DFT. A dynamical extension is also possible through the time-dependent DFT (Deb and Ghosh 1982; Runge and Gross 1984; Bartolotti 1986; Dhara and Ghosh 1987) which gives new insight into the collision phenomena (Deb and Chattaraj 1987).

The PS approach in general can be very helpful in understanding the connections between classical and quantum mechanics. Here a dynamical variable is represented by an ordinary function of $\mathbf{r}$ and $\mathbf{p}$ and the quantum mechanical averages are evaluated just like in a classical case. Another distinctive feature is that both the state and the transition can be handled in an equivalent manner. The PS formalism is also useful in deriving the equations of quantum fluid dynamics (Deb and Ghosh 1987).

The DFT in terms of $\rho(\mathbf{r})$ is well established and sufficient interest is generated for DFT in momentum space as well in terms of $\gamma(\mathbf{p})$. An alternative formulation of DFT is however possible in phase space in terms of $f(\mathbf{r}, \mathbf{p})$; this might be of special importance in dealing with time-dependent phenomena. The understanding of chemical binding is considerably enhanced through studies of contour maps of electron density (Bamzai and Deb 1981) as well as momentum density (Koga *et al* 1985 and references therein). Studies on $f(\mathbf{r}, \mathbf{p})$ for simple atomic (Dahl and Springborg 1982) and molecular (Springborg 1983) systems have started only recently and seem to be a valuable approach for understanding physicochemical phenomena.

Acknowledgements

It is a pleasure to thank Professors Robert G Parr and Max Berkowitz for many helpful discussions. I am grateful to Professor B M Deb for his constant encouragement and advice.

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A viable alternative to the unitary group approach in quantum chemistry

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Abstract. A certain element of danger of the unitary group approach and practice is pointed out. A viable alternative formalism is presented with an overview of the development, a summary of the achievements and a discussion on its prospects pertaining to the configuration interaction calculations, open-shell perturbation theory, propagator methods and variational theory. Special reference is given to the open-shell HF problem. Lastly, the possibility of handling atomic multiplet states is discussed.

Keywords. Unitary group approach; electronic structure; open-shell theory; multiconfigurational propagator.

1. Introduction

In spite of the remarkable success of the unitary group techniques in quantum chemistry (Paldus 1981; Shavitt 1981) it may not be entirely pointless to welcome an alternative approach which, on one hand, would be as viable as the unitary group-based methods are as far as their technical achievement is concerned, and on the other, would not, like these methods, pose any threat to conceptual developments in quantum chemistry. Indeed, the unitary-group derived approach, by providing a computational "blackbox", will soon have set the trend among quantum chemists to use it indiscriminately on a "feed and extract" basis, and with time, there will be no room for the play of imagination and the exercise of intuition in quantum chemistry.

Here we bring a progress report of one formulation (Mukhopadhyay and Pickup 1982) which is viable in the above sense, and provides a meaningful language in which a quantal electronic structure problem can be conceived, formulated and solved without having to undergo any technical drudgery.

2. Formulation

We begin by asking what the unitary group is set to achieve in a problem of the above nature. Addressing a general open-shell system where it really triumphs, it basically purports to generate the various electronic states and the corresponding Hamiltonian matrix, and to evaluate the latter, all very efficiently. For the latter aspect, it is rewarding to classify the states according to their behaviour under spin

and other symmetries of the Hamiltonian. Let us first tackle the spin problem the way we want to, the rest follows quite easily.

A general open-shell means a distribution of a certain number of electrons in several orbital-levels with varied occupancies 0, 1 or 2 *outside* a closed-shell core of doubly occupied levels. The latter is easily given a state, necessarily a spin-singlet, as a sequential product of the Fock-space pair creation operators $\mathbf{P}_i$, $i(j, k, \dots)$ referring to the closed-shell orbitals:

$$|0\rangle = \prod_j^{N_c/2} \mathbf{P}_{i_j} |\text{vac}\rangle, \quad \langle 0|0\rangle = 1, \quad \mathbf{P}_i = X_{i\beta}^+ X_{i\alpha}^+, \quad (1)$$

N_c being the number of electrons in the core, $|\text{vac}\rangle$ the no-orbital singlet vacuum state, and $X_{i\beta}^+$ ($X_{i\alpha}$) the fermion spin-orbital creation (annihilation) operators. By the Pauli exclusion principle, no two P operators in the same spin state may have identical labels.

To account for the distribution over the remaining, so-called open-shell levels ($u, v, w, \dots$), we introduce, in addition to $\mathbf{P}_u$, two other Fock-space operators:

$\mathbf{U}_u(S)$, which, acting on an arbitrary many-electron spin state $|S\rangle$ where the orbital u is empty, creates an electron in orbital u , and increases the spin of the resulting state by $\frac{1}{2}$;

$\mathbf{D}_u(S)$, which, similarly acting, decreases the spin by $\frac{1}{2}$. Since spin cannot be lowered below $S = 0$, we demand that

$$\mathbf{D}_p |S = 0\rangle = 0, \quad \text{for any orbital } p(q, r, \dots). \quad (2)$$

With all that we have, any many-electron spin state, normalized to unity, can be written down as a sequential product of the above three types of creation operators acting on a vacuum. Figure 1 describes the spin states in the genealogical scheme (see Pauncz 1979) with $N_c + 3$ electrons. Each spin state is a linear combination of several Slater determinants, and the combining coefficients, if necessary, are easily retrieved as shown in Mukhopadhyay and Pickup (1982).

The annihilation operators corresponding to $\mathbf{P}_p$, $\mathbf{U}_p$ and $\mathbf{D}_p$ are not $\mathbf{P}_p^+$, $\mathbf{U}_p^+$ and $\mathbf{D}_p^+$, respectively, but the related operators $\mathbf{P}^p$, $\mathbf{D}^p$ and $\mathbf{U}^p$ to within some unimportant factors, and their effect on a given spin state is to remove an electron (electrons, if it is P) occupying the orbital p therein, changing the spin as implied in the notation: U for "up" increases, D for "down" decreases, and P for "preserve" maintains. Diagrammatically, a bra spin state obtains by reflecting the corresponding ket spin state diagram in a vertical mirror, and reversing the arrows as explained in the box part of figure 1.

One can dispense with the core by treating it as the new vacuum $|0\rangle$, and proceed by particle-hole transforming the above operators. Deleting the underbars for the transformed operators, the new vacuum is fixed by

$$\mathbf{D}^p |0\rangle = 0 = \mathbf{U}^p |0\rangle, \quad \text{for all } p. \quad (3)$$

The algebra carried by these spin-adapted creation and annihilation operators (Pickup and Mukhopadhyay 1984a; Mukhopadhyay and Pickup 1984) is decided partly by the behaviour of two-electron states under orbital transposition; this is best accounted for by recognising only six distinct crossings between the creation and/or annihilation operators (cf figure 2A). The algebra is completed by the

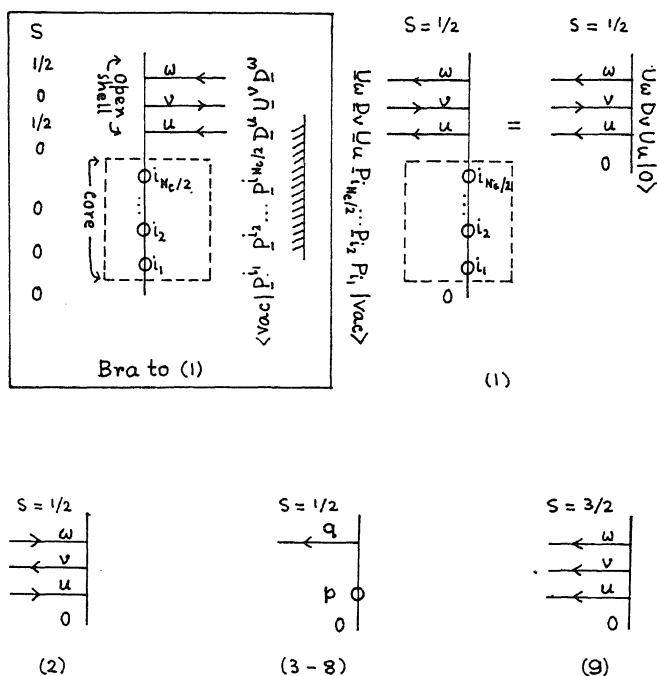


Figure 1. Spin-state diagrams showing $S = \frac{1}{2}$ (1-8) and $S = \frac{3}{2}$ (9) kets. Formation of bra to (1) is shown inside the box; S in the leftmost column stands for the segmental spin values. Six diagrams (3-8) may be generated by allowing p, q the values u, v , and w .

orthonormality among the spin states generated (provided the orbital basis is orthonormal which we have assumed), and this is ensured by resorting to a set of contraction rules as in figure 2B. The permutational behaviour takes care of the Pauli exclusion principle, for no two lines in a given spin state, having arrows in the same direction, can bear the same labels.

From the algebra implied by figure 2A it is not difficult to pass from the genealogical to the Jahn-Serber coupling scheme as will be shown elsewhere (Mukhopadhyay and Pickup 1987). This necessitates diagonalization of the matrix of the transposition (p, q) over the two-electron genealogical basis $U_q U_p$, $U_q D_p$, $D_q U_p$ and $D_q D_p$ all acting on an arbitrary spin state. For the rest of the paper, however, we stick to the genealogical basis.

The much-occurring spin-independent Hamiltonian

$$H' = H - \langle 0 | H | 0 \rangle = \sum_{p,q} \langle p | f | q \rangle N[E_{pq}] + \frac{1}{2} \sum_{p,q,r,s} \langle pq | v | rs \rangle N[E_{pr} E_{qs}] \quad (4)$$

is easily shown to have a diagrammatic representation (Mukhopadhyay and Pickup 1982, 1984) given and explained in figure 3. The term $\langle 0 | H | 0 \rangle$ represents the core energy, $N[E_{pq}]$ normal ordering with respect to $|0\rangle$, and $E_{pq} = \sum_{\sigma} X_{p\sigma}^+ X_{q\sigma}$ is the orbital unitary group generator, σ assuming α or β spin. f refers to the

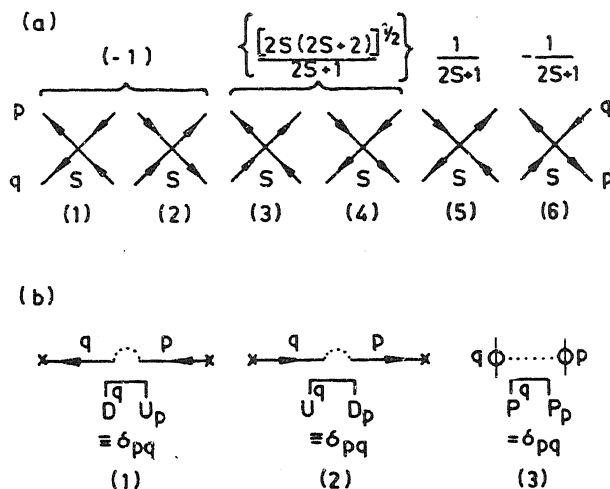


Figure 2. Algebra of the spin-adapted operators. (a) Six distinct crossings are shown, each conserving afrow current and having a value shown at the top with reference to the segmental spin value at the bottom. Relations induced by the orbital transposition (p, q) like

$$D_q U_p |S\rangle = \{1/(2S+1)\} D_p U_q - \{[2S(2S+2)]^{1/2}/(2S+1)\} U_p D_q |S\rangle$$

may be obtained from (3) and (5) which have identical right hand parts. (b) Only allowed contractions are shown, omitting some unimportant factors; lines with matching arrows are contracted.

Hartree-Fock (HF) operator defined with respect to the core not necessarily satisfying

$$\langle p | f | q \rangle = \varepsilon_p \delta_{pq}. \quad (5)$$

The greatest virtue of the present formulation is apparent when we come to form and evaluate matrix-elements of the Hamiltonian over the spin states; one generates a matrix-element diagram in almost the same manner as in the standard many-body theory (cf figure 4). One notable difference is contained in this: a circle and a line may now be contracted as shown in the inset of figure 4. Evaluation proceeds via the following rules:

1. draw only the topologically distinct matrix-element diagrams, that is, the ones which do not, under allowed deformation, pass into one another;
2. evaluate all the L -shapes (cf figure 4): a clockwise L -shape gets a factor $L_c(S) = \sqrt{\{(2S+2)/(2S+1)\}}$ whereas an anticlockwise L -shape gets $L_a(S) = -\sqrt{\{(2S)/(2S+1)\}}$, S being the segmental spin below the apex of the L -shape;
3. evaluate all the crossings according to figure 2A;
4. associate orbital matrix-elements to all the F and V vertices in the diagram (cf figure 3);

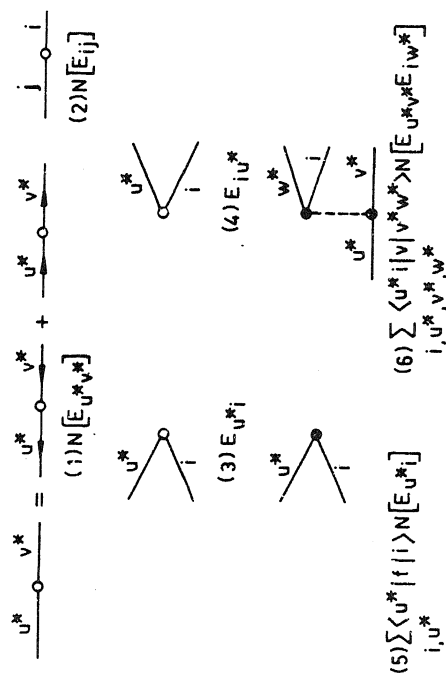


Figure 3. Hamiltonian diagrams involving E (1–4) apart from some implicit factors, a typical F (5) and V (6). Note the way orbital matrix-elements are associated. (1) also explains the convention adopted; arrow current must be conserved.

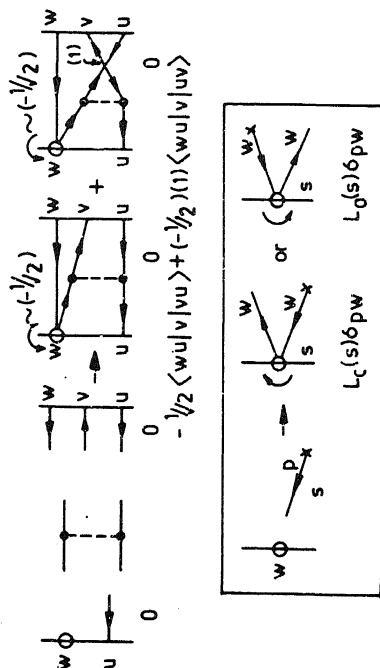


Figure 4. Formation of a typical matrix-element diagram. The box part explains what happens when a pair and any annihilation/creation operator (either from an E or from a state indicated by an x at the end) are involved: either a clockwise or an anticlockwise L-shape obtains having a value $L_c(S)$ or $L_a(S)$, respectively.

5. ascribe a phase of (-1) to every hole-hole scattering in a vertex;
6. give a topological factor of $1/2$ to every V vertex that has a mirror plane within the matrix-element diagram;
7. multiply out.

These rules are akin to the ones we are used to in the ordinary many-body theory, and are far simpler than those prescribed in the unitary-group derived methods. It should be possible to exploit this simplicity algorithmically to compete with the unitary group in effecting configuration interaction calculations.

3. Further developments and prospects

Implementation of open-shell perturbation theory in the unitary group framework (Shavitt 1981) faces an organizational difficulty in properly selecting the subspace of the configuration functions. While this might require a redressing of the entire configuration space, relevance and efficacy of the present formulation is discussed in Mukhopadhyay and Pickup (1984).

The other important area where this formalism has proved its worth concerns the propagator theory. In the traditional open-shell formulation (Linderberg and Öhrn 1973; Albertsen and Jørgensen 1979) it is impossible to distinguish poles of a non-singlet propagator of one-spin symmetry from those of others. In an earlier variant, the present formalism led to a successful decoupling, thus isolating the triplet pole from the singlet one (Pickup and Mukhopadhyay 1981). An interesting application of this work appears in Nichols *et al* (1984) where the authors not only make assignments of some shake-up peaks in the PES and ESCA spectra of O_2 but also predict location of some others. Further extensive work is necessary till we resolve the problems of multiconfigurational propagator theory satisfactorily, though certain progress has been made in this direction (Pickup and Mukhopadhyay 1984b). Success of the unitary group in this context (Born and Shavitt 1982) will depend on how the basic structure of the associated approach has to be revised.

To indicate applicability of the formalism in variational theories let us consider the issue of the HF solutions for a simple open-shell system having one electron outside the core. Naturally we would write the trial ground state function as

$$|\varphi\rangle = U_u|0\rangle, \langle\varphi|\varphi\rangle = 1. \quad (6)$$

A necessary condition for the expectation value of H' in (4) is that

$$\langle\delta\varphi|H'|\varphi\rangle = 0 \text{ to first order in } \langle\delta\varphi| \text{ for all orbitals.} \quad (7)$$

A first-order change in $|\varphi\rangle$ is effected by replacing the orbital u by $u + \xi a$ and the core orbital i by $i + \rho u^*$ where ξ and ρ are two small numbers, a an orbital not occupying $|\varphi\rangle$ and u^* an orbital outside the core. This induces the following first-order change in $|\varphi\rangle$:

$$|\delta\varphi\rangle = (\xi U_a D'' + \rho U_u \cdot D_i) |\varphi\rangle = (\xi U_a D'' + \rho U_u \cdot D_i) U_u |0\rangle. \quad (8)$$

The condition (7) would then require fulfilment of

$$\langle 0 | D^i U''^* D'' H' U_u | 0 \rangle = 0, \text{ for } u, \text{ and all } i, a, \quad (9)$$

and simultaneously of

$$\langle 0 | D'' H' U_u | 0 \rangle = 0, \text{ for } u \text{ and all } a. \quad (10)$$

These are the Brillouin conditions (Lefebvre 1965). Evaluating these from the corresponding diagrams in figure 5 according to the rules given earlier we have (Paldus and Čížek 1970),

$$\langle u | f | i \rangle + \langle uu | v | ui \rangle = 0, \text{ when } u^* \text{ is } u, \quad (11)$$

$$2\langle a | f | i \rangle + \langle ua | v | ui \rangle - \langle ua | v | iu \rangle = 0, \text{ when } u^* \text{ is } a, \quad (12)$$

$$\langle a | f | u \rangle = 0 \quad (13)$$

for u , and all i, a ; here f corresponds to the core HF operator.

Searching for a set of Brillouin conditions for a general open-shell case would certainly be an interesting problem to pursue. By carrying out an analysis of the above type up to second-order variation one can also address the associated stability problems.

Lastly we discuss how atomic multiplet states may be handled. Let us consider the p^3 configuration of an atom, and suppose 1, 2 and 3, respectively, stand for the orbital states $|nl = 1, m_l\rangle$ with $m_l = 1, 0, -1$. The possible spin states may be recovered from figure 1 by letting u, v, w assume labels 1, 2 and 3. The total M_L value of each spin state is easily obtained by adding up the m_l values of the orbitals occupying the open-shell levels. For a given S it is thus possible to locate the spin state that has the highest M_L , say M_L^h ; it is then the multiplet state ^{2S+1}L , L being M_L^h . The other LS states with different M_L values may be obtained by successive application of the lowering operator L_- which, in the present case, is proportional

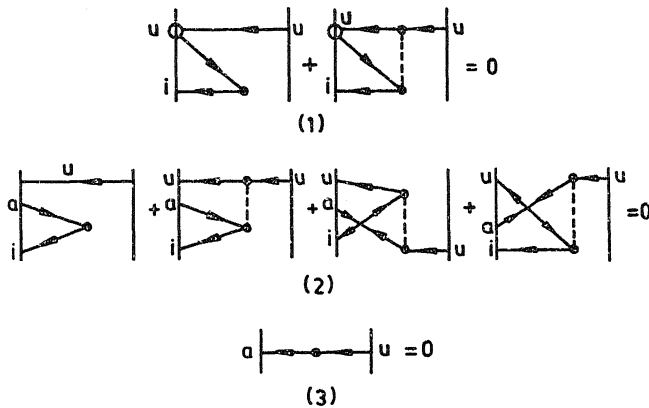


Figure 5. The Brillouin conditions for a simple open shell. Single excitations in (1) is from i to u forming a pair in the latter, in (2) from i to a , and in (3) from u to a ; all excitations retain the singlet character of the core state.

$$\begin{aligned}
 |^2D \quad 2\rangle &= \begin{array}{c} \rightarrow \\ \phi_1^2 \end{array} \\
 |^2D/2p \quad 1\rangle &= \frac{1}{2} \left(\begin{array}{c} \rightarrow \\ \phi_1^3 \end{array} + \begin{array}{c} \rightarrow \\ \phi_1^2 \end{array} \right) \\
 |^{\dots} \quad 0\rangle &= \frac{\sqrt{3}}{2} \begin{array}{c} \rightarrow \\ \phi_2^3 \\ \rightarrow \\ \phi_1^2 \\ \rightarrow \\ \phi_1 \end{array} + \frac{1}{2} \begin{array}{c} \rightarrow \\ \phi_2^3 \\ \rightarrow \\ \phi_1^2 \\ \rightarrow \\ \phi_1 \end{array} \\
 |^{\dots} \quad -1\rangle &= \frac{1}{2} \left(\begin{array}{c} \rightarrow \\ \phi_3^1 \end{array} + \begin{array}{c} \rightarrow \\ \phi_3^2 \end{array} \right) \\
 |^2D \quad -2\rangle &= \begin{array}{c} \rightarrow \\ \phi_2^3 \end{array}
 \end{aligned}$$

$$\begin{aligned}
 \{\hat{L}_{-}(E_{21}+E_{32})\} \begin{array}{c} \rightarrow \\ \phi_1^2 \end{array} &= \begin{array}{c} \rightarrow \\ \phi_2^2 \end{array} + \begin{array}{c} \rightarrow \\ \phi_1^2 \end{array} \\
 &= \left(- \begin{array}{c} \rightarrow \\ \phi_1^2 \end{array} + \begin{array}{c} \rightarrow \\ \phi_1^3 \end{array} \right) \rightarrow \frac{1}{2} \left(- \begin{array}{c} \rightarrow \\ \phi_1^2 \end{array} + \begin{array}{c} \rightarrow \\ \phi_1^3 \end{array} \right)
 \end{aligned}$$

Figure 6. Atomic spin angular momentum states $|^{2S+1}LM_L\rangle$ of a p^3 configuration. The box part explains the steps from the first to the second line. In the second to fourth lines 2D (2P) corresponds to the upper (lower) sign.

to $\Sigma_p E_{p+1,p}$, the proportionality constant being fixed by normalizing the resulting state to unity. Other multiplet states are obtained in the usual manner by orthogonalization, and the results appear in figure 6. Formulation of this kind lends an easy means of obtaining coefficients of fractional parentage of open-shell systems and exploring their relevance to X-ray PES studies (Mukhopadhyay 1987).

4. Concluding remarks

Once the pertinent symmetries are taken care of in a formulation without upsetting the structure akin to the standard many-body theory, much of the open-shell developments may take place as easily as in relatively simpler problems. A study of multiconfigurational self-consistent field theory in this formalism may be one test-case.

There is considerable group theoretical work behind what is presented here, and this ensures the properties of the spin-adapted operators to be as reported, guaranteeing at the same time, the cancellation of the various factors frequently swept aside as unimportant. The rules are what the formalism eventually amounts to; they are simple and accessible even to those who do not know anything about the unitary group or the Racah algebra.

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Radiative interactions in diatomic molecules

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Abstract. Radiative interactions which give rise to allowed and forbidden radiative transitions in diatomic molecules are presented as tensor operators. A translational expansion of these interaction operators from the centre of mass of the molecule to the atomic centres is discussed. It is found that the expansion of the magnetic dipole interaction operator generates an extra gradient operator which may contribute significantly towards the transition probability. The expansion of atomic orbitals from one centre to the other is also discussed and analytical expressions of the two-centre integrals which one may encounter in radiative processes are presented.

Keywords. Tensor operators; translational expansion; gradient operator; two-centre integrals.

1. Introduction

The interaction of diatomic molecules with an electromagnetic field involves clear understanding of the molecular wavefunctions and angular momenta. Since the angular momenta of the molecule obey reverse commutation rules with respect to molecule-fixed axes (Van Vleck 1951), care has to be taken in studying the molecule-field interaction problems. By virtue of the multipole expansion of the radiation field, the interaction operators refer to the space-fixed axis whose origin lies at the centre of mass of the molecule. The molecular angular momenta and wavefunctions, on the other hand, are given with respect to the molecule-fixed co-ordinate system. Hence, for calculation, a transformation of the operators from the space-fixed system to the molecule-fixed system or vice versa becomes necessary. Besides, if the electronic wavefunctions are presented in terms of atomic orbitals at nuclear sites and the operators refer to the centre of mass of the molecule, the electronic transition moment involves multi-centre integrals. To calculate them correctly, a translational expansion of the operators and orbitals from one centre to the other becomes essential. In this paper, we discuss transition in diatomic molecules by radiative interactions. Though the advent of fast computers have made the evaluation of matrix elements simpler even with complicated many-term wavefunctions, analytical expressions will always be welcome for wavefunctions and matrix elements. We shall try to achieve such analytical expressions wherever possible.

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2. The Born-Oppenheimer separation

For simplicity, we discuss this separation for a Hund's case (b) diatomic molecule (Herzberg 1950) where spin-internuclear axis interaction is relatively weak. $\Psi(x_\rho, y_\rho, z_\rho, R, \beta, \alpha, s_\rho)$ is taken as the total wavefunction for a Hund's case (b) molecule, $\rho = 1, 2, \dots, n$. (x_j, y_j, z_j) and (ξ_j, η_j, ζ_j) will be used as positional co-ordinates of the j th electron with respect to the space-fixed system (XYZ) and the molecule-fixed co-ordinate system $(\xi\eta\zeta)$, respectively. We let the centre of mass of the nuclei be at rest at the origin of the co-ordinate systems (XYZ) and $(\xi\eta\zeta)$ which is the rotated frame work of (XYZ) by virtue of the right-handed rotations through Euler angles $(\alpha\beta\gamma)$ (Rose 1961). The ζ -axis coincides with the molecular axis. Only two rotations (α, β) are sufficient to explain the orientation of a diatomic molecule (rigid-rotor type) in space. We may also introduce spin co-ordinates for electrons: s_j when they are related to the individual spin-axis and σ_j when the ζ -axis is chosen as the reference axis.

The exact Hamiltonian operator may be written as

$$H = -\frac{\hbar^2}{2\mu R^2} \left[\frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{\sin \beta} \frac{\partial}{\partial \beta} \left(\sin \beta \frac{\partial}{\partial \beta} \right) + \frac{1}{\sin^2 \beta} \frac{\partial^2}{\partial \alpha^2} \right] - \frac{\hbar^2}{2m} \sum_j \nabla^2(x_j, y_j, z_j) + V_{nn}(R) + V_{ee, en}(x_\rho, y_\rho, z_\rho; R, \beta, \alpha) + W(s_\rho), \quad (1)$$

where the first and second terms represent the kinetic energies of the nuclei and electrons, respectively. $V_{nn}(R)$ is the potential energy arising from nuclear interaction and $V_{ee, en}$ comprises of ordinary electron-electron and electron-nuclear Coulomb potentials. Here m is the electronic mass, μ the reduced mass and R is the internuclear distance. We have added the spin-dependent interaction term $W(s_\rho)$ in the Hamiltonian.

To express both H and Ψ relative to the moving figure axis (Judd 1975; Chiu 1964), we transform the positional co-ordinates as follows:

$$\begin{pmatrix} \xi_j \\ \eta_j \\ \zeta_j \end{pmatrix} = \begin{pmatrix} \cos \alpha \cos \beta & \sin \alpha \cos \beta & -\sin \beta \\ -\sin \alpha & \cos \alpha & 0 \\ \cos \alpha \sin \beta & \sin \alpha \sin \beta & \cos \beta \end{pmatrix} \begin{pmatrix} x_j \\ y_j \\ z_j \end{pmatrix}, \quad (2)$$

and the differential operators in the two co-ordinate systems are now related as

$$\begin{aligned} (\partial/\partial\beta)_{\text{space}} &= (\partial/\partial\beta)_{\text{mol}} - iL_\eta, \\ (\partial/\partial\alpha)_{\text{space}} &= (\partial/\partial\alpha)_{\text{mol}} + iL_\xi \sin \beta - iL_\zeta \cos \beta, \end{aligned} \quad (3)$$

where L_ξ, L_η, L_ζ represent the components of the angular momentum of the electron in the moving co-ordinate system $(\xi\eta\zeta)$ in units of $\hbar$. With these transformations, the Schrodinger equation becomes,

$$\begin{aligned}
& \left\{ H_e(\xi_\rho, \eta_\rho, \zeta_\rho, R, s_\rho) - B \left[\frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \right. \right. \\
& + \frac{1}{\sin \beta} \left(\frac{\partial}{\partial \beta} - iL_\eta \right) \sin \beta \left(\frac{\partial}{\partial \beta} - iL_\eta \right) \\
& + \frac{1}{\sin^2 \beta} \left(\frac{\partial}{\partial \alpha} + iL_\xi \sin \beta - iL_\xi \cos \beta \right)^2 \left. \right] \\
& + V_{nn}(R) - E \left. \right\} \Psi(\xi_\rho, \eta_\rho, \zeta_\rho, R, \beta, \alpha, s_\rho) = 0, \quad (4)
\end{aligned}$$

where

$$H_e = -\frac{\hbar^2}{2m} \sum_j \nabla^2(\xi_j, \eta_j, \zeta_j) + V_{ee,en}(\xi_\rho, \eta_\rho, \zeta_\rho, R) + W(s_\rho), \quad (5)$$

and $B = \hbar^2/2\mu R^2$.

In the Born-Oppenheimer separation, we assume that the electronic problem with the fixed nuclei is solved. And, with the omission of a few interaction terms, the total molecular wavefunction Ψ can be separated into electronic ϕ^e , rotational $\Theta(\alpha, \beta)$ and radial $P(R)$ wavefunctions, which are solutions of the following differential equations:

$$\begin{aligned}
& [H_e(\xi_\rho, \eta_\rho, \zeta_\rho, R, s_\rho) - E_e(R)] \phi^e(\xi_\rho, \eta_\rho, \zeta_\rho, R, s_\rho) = 0, \\
& B \left[\cot \beta \frac{\partial}{\partial \beta} + \frac{\partial^2}{\partial \beta^2} + \frac{1}{\sin^2 \beta} \left(\frac{\partial}{\partial \alpha} - i\Lambda \cos \beta \right)^2 \right] \Theta(\alpha, \beta) + E_{\text{rot}} \Theta(\alpha, \beta) = 0, \\
& \left[B \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - E_e(R) - V_{nn}(R) - E_{\text{rot}} - \bar{U}(R) + E \right] P(R) = 0. \quad (6)
\end{aligned}$$

In deriving the above equations, the conditions,

$$L_\xi \phi^e = \Lambda \phi^e,$$

$$\text{and} \quad \langle \phi^e | L_\xi | \phi^e \rangle = \langle \phi^e | L_\eta | \phi^e \rangle = 0, \quad (7)$$

have been imposed. Λ , the electronic angular momentum along the internuclear axis is measured in units of $\hbar$. $\bar{U}(R)$ appearing in the radial equation is defined as:

$$\bar{U}(R) = B \left\langle \phi^e \left| L_\xi^2 + L_\eta^2 - \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - \frac{2R^2}{P} \frac{\partial}{\partial R} P \frac{\partial}{\partial R} \right| \phi^e \right\rangle. \quad (8)$$

The total wavefunction for a Hund's case (b) symmetric top diatomic molecule at a particular rotational level N may be expressed as:

$$\Psi_{Nm\Lambda v m_\gamma} = P_v(R) \Psi_{Nm\Lambda}(\xi_\rho, \eta_\rho, \zeta_\rho, R, \alpha, \beta, \gamma) \chi_{s, m_\gamma}(s_\rho), \quad (9)$$

where $\Psi_{Nm\Lambda}$ is the electronic-rotational wavefunction, which may again be expressed as (Bhattacharyya and Chiu 1977)

$$\Psi_{Nm\Lambda}^\pm = \left[\frac{2N+1}{16\pi^2} \right]^{1/2} [\mathcal{D}_{m\Lambda}^{N*}(\alpha\beta\gamma) \phi_\Lambda^e \pm (-1)^N \mathcal{D}_{m, -\Lambda}^{N*}(\alpha\beta\gamma) \phi_{-\Lambda}^e] \quad (10)$$

where $\mathcal{D}_{m\Lambda}^N$ is the rotation matrix element (Brink and Satchler 1962). The quantum numbers m and Λ are components of the angular momentum $N\hbar$ along the fixed

Z-axis and the moving figure-axis respectively. The $\pm$ sign refers to the eigenvalue ± 1 under inversion operation. States $+\Lambda$ and $-\Lambda$ are degenerate and are called Λ -doublets.

3. Radiative interaction operators

The operators causing radiative interactions may be expressed as tensor operators (Brink and Satchler 1962) so that the matrix elements of these operators may be evaluated by using the Racah algebra. We consider absorption or emission of a single photon of energy $\hbar c k_\lambda$ and after separating the photon part, the Hamiltonian $H(\mathbf{r}, \lambda)$ which operates on the molecular system only is given by a sum of the spin-independent part of the interaction:

$$H_r(\mathbf{r}, \lambda) = -\left(\frac{e}{2mc}\right) \sum_i [\mathbf{A}_\lambda^*(\mathbf{r}_i) \cdot \mathbf{p}_i + \mathbf{p}_i \cdot \mathbf{A}_\lambda^*(\mathbf{r}_i)], \quad (11)$$

and the spin-dependent part of the interaction:

$$H_s(\mathbf{r}, \lambda) = -\left(\frac{e}{2mc}\right) \sum_i 2\hbar \mathbf{s}_i \cdot \nabla \times \mathbf{A}_\lambda^*(\mathbf{r}_i). \quad (12)$$

Here e and m are respectively electronic charge and mass, c is the velocity of light, $\mathbf{p}_i$ and $\mathbf{s}_i$ are the linear momentum and spin of the electron i respectively. $\mathbf{A}_\lambda(\mathbf{r}_i)$ is the vector potential of the transverse electromagnetic field that interacts with the charged particle.

By Taylor's expansion of $\mathbf{A}_\lambda^*(\mathbf{r}_i)$, we can obtain the multipole expansion of $H(\mathbf{r}, \lambda)$ (Brink and Satchler 1962; Chiu 1966):

$$H(\mathbf{r}, \lambda) = -\sum_{lm} \frac{i^l k_\lambda^l}{(2l-1)!!} \left(\frac{l+1}{2l}\right)^{1/2} \mathcal{Q}_{lmq}^l(\hat{R}) \{(\varepsilon_{lm} + \varepsilon'_{lm}) - iq(M_{lm} + M'_{lm})\}, \quad (13)$$

where $q = \pm 1$ are the transverse polarisations, ε_{lm} and ε'_{lm} are the electric multipole operators of parity $(-1)^l$ contributed by electronic charge and electron spin respectively. Similarly M_{lm} and M'_{lm} are the magnetic multipole operators of parity $(-1)^{l+1}$ contributed respectively by electronic charge and electron spin. The leading terms in the spin-independent interaction $H_r(\mathbf{r}, \lambda)$ and $H_q(E 1)$, the electric-dipole interaction, $H_q(M 1)$, the magnetic-dipole interaction with even parity and $H_q(E 2)$, the electric-quadrupole interaction with even parity. They are expressed as tensor operators in the following way:

$$\begin{aligned} H_q(E 1) &= -ik_\lambda e \sum_{jm} \mathcal{D}_{mq}^1(\hat{R}) r_j c_m^1(\hat{r}_j), \\ H_q(E 2) &= (ek_\lambda^2/2\sqrt{3}) \sum_{jm} \mathcal{D}_{mq}^2(\hat{R}) r_j^2 c_m^2(\hat{r}_j), \\ H_q(M 1) &= -k_\lambda q \mu_\beta \sum_{jm} \mathcal{D}_{mq}^1(\hat{R}) L_m^1(\hat{r}_j). \end{aligned} \quad (14)$$

In the above equations, $\mu_\beta = e\hbar/2mc$ is the Bohr magneton, $C_m^l(\hat{r}_j) = [4\pi/(2l+1)]^{1/2} Y_{lm}(\hat{r}_j)$ is the modified spherical harmonics, $\hat{r}_j = (\theta_j, \phi_j)$ and $\mathbf{r}_j$ are

referred to the centre of mass of the molecule in a space-fixed coordinate system. $\mathcal{D}_{mq}^l(\hat{R})$ is the rotation matrix element where $\hat{R} = (\alpha, \beta, \gamma)$ are the Euler angles which take the space-fixed quantisation axis into the direction of the propagation vector $\mathbf{K}_\lambda$, and

$$L_{\pm 1}^1(\mathbf{r}_j) = \mp \frac{1}{(2)^{1/2}} (L_{xj} \pm iL_{yj}), \quad L_0^1(\mathbf{r}_j) = L_{zj} \quad (15)$$

are the angular momentum operators expressed as tensors.

The spin-dependent Hamiltonian $H_s(\mathbf{r}, \lambda)$ comprises primarily of spin-dependent electric-dipole interaction $H_q(SE\ 1)$ and spin-dependent magnetic-quadrupole interaction $H_q(SM\ 2)$ which can be expressed as:

$$\begin{aligned} H_q(SE\ 1) &= 2^{1/2} i k_\lambda^2 \mu_\beta \sum_{jmv} \mathcal{D}_{mq}^1(\hat{R}) c(111; m - \nu \nu m) r_j c_{m-\nu}^1(\hat{r}_j) s_\nu(j), \\ H_q(SM\ 2) &= -2^{1/2} i q k_\lambda^2 \mu_\beta \sum_{jmv} \mathcal{D}_{mq}^2(\hat{R}) c(112; m - \nu \nu m) r_j c_{m-\nu}^1(\hat{r}_j) s_\nu(j). \end{aligned} \quad (16)$$

These are interactions with odd parity and can induce forbidden singlet-triplet transition (Mizushima 1964). $C(\dots)$ in the above is the Clebsch-Gordan coefficient (Rose 1961).

4. Translational expansion of interaction operators and atomic orbitals

In the evaluation of electronic transition moments (after separating the rotational and vibrational parts) of a diatomic molecules, one generally encounters single-electron two-centre integrals of the following type:

$$\langle g(\mathbf{r}_a) | M(\mathbf{r}) | h(\mathbf{r}_b) \rangle \quad \text{and} \quad \langle g(\mathbf{r}_a) | M(\mathbf{r}) | h(\mathbf{r}_a) \rangle, \quad (17)$$

and also other integrals by interchanging a and b . Here $g(\mathbf{r}_a)$ and $h(\mathbf{r}_b)$ are atomic orbitals centred at nuclei a and b respectively, and $M(\mathbf{r})$ is the radiative operator at the centre of mass. The integrals will have to be evaluated at a particular nuclear site or at the centre of mass. We, therefore, have to make a translational expansion of the operators, originally at the centre of mass, at nuclear sites a and b . Similarly, the atomic orbitals at a and b may also be expanded at other sites.

For this expansion, we may choose a coordinate system for centre a , centre b and the centre of mass (figure 1) so that

$$x_a = x_b = x, \quad y_a = y_b = y, \quad z_a = z + R/2 \quad \text{and} \quad z_b = z - R/2, \quad (18)$$

where R is the internuclear distance. Making use of these relations, the electric-dipole and electric-quadrupole operators can be expanded from the centre of mass of the molecule to the atomic centres a and b . Thus,

$$r^l c_m^l(\hat{r}) = \sum_{\sigma=|m|}^l \xi_\alpha^{l-\sigma} \frac{(R/2)^{l-\sigma}}{(l-\sigma)!} \left[\frac{4\pi(l-m)!(l+m)!}{(2\sigma+1)(\sigma-m)!(\sigma+m)!} \right]^{1/2} r_\alpha^\sigma Y_{\sigma m}(\hat{r}_\alpha), \quad (19)$$

where α refers to either centre a or centre b . Here $\xi_a = -1$ and $\xi_b = 1$. Setting

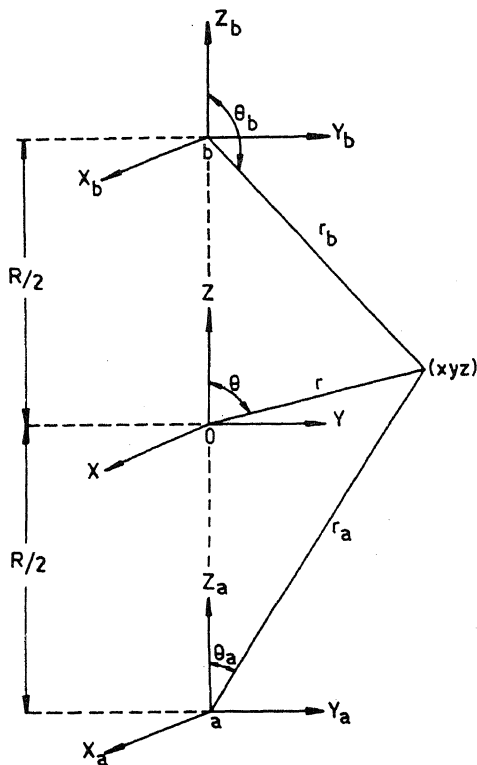


Figure 1. The coordinate systems for centre a , centre b and the centre of mass are all right-handed.

$l = 1$ and $l = 2$ in the above equation, we get in terms of tensors the expansion of electric-dipole and electric-quadrupole operators and so on. This expansion is quite in agreement with that derived from Hobson's formula (Hobson 1931; Chiu 1977).

With the same relations as in (18), the individual components L_x, L_y, L_z can be translationally expanded from the centre of mass to atomic site α , and the operators $L_{\pm 1}^1$ and L_0^1 appearing in magnetic-dipole interaction become

$$\begin{aligned} L_{\pm 1}^1(\mathbf{r}) &= L_{\pm 1}^1(\mathbf{r}_\alpha) \pm \xi_\alpha(R/2) \nabla_{\pm 1}^1(\mathbf{r}_\alpha), \\ L_0^1(\mathbf{r}) &= L_0^1(\mathbf{r}_\alpha), \end{aligned} \quad (20)$$

where $\nabla_{\pm 1}^1(\mathbf{r}_\alpha) = \mp (1/\sqrt{2})(\partial/\partial x_\alpha \pm i\partial/\partial y_\alpha)$ is the gradient operator (also a tensor operator) at atomic centre α . The above equation gives essentially a translational expansion of the magnetic-dipole interaction operator whereby an additional gradient operator $\nabla_{\pm 1}^1$ is generated. Applying the gradient formula (Rose 1961), we obtain the result of operating $L_{\pm 1}^1(\mathbf{r})$ on the atomic orbital of angular momentum l and centred at nucleus α :

$$\begin{aligned} L_{\pm 1}^1(\mathbf{r}) \phi(\mathbf{r}_\alpha) Y_{lm}(\hat{r}_\alpha) &= [l(l+1)]^{1/2} c(l \ 1 \ l; m \ \pm 1 \ m \ \pm 1) \phi(\mathbf{r}_\alpha) Y_{l, m \pm 1}(\hat{r}_\alpha) \\ &\pm (R/2) \xi_\alpha \left[\left(\frac{l+1}{2l+1} \right)^{1/2} \left(\frac{d\phi}{dr_\alpha} - \frac{l}{r_\alpha} \phi \right) c(l+1 \ 1 \ l; m \ \pm 1 \ \mp 1 \ m) Y_{l+1, m \pm 1}(\hat{r}_\alpha) \right. \end{aligned}$$

$$- \left(\frac{l}{2l+1} \right)^{1/2} \left(\frac{d\phi}{dr_\alpha} + \frac{l+1}{r_\alpha} \phi \right) c(l-1 \ 1 \ l; m \pm 1 \mp 1 \ m) Y_{l-1, m \pm 1}(\hat{r}_\alpha) \Big], \quad (21)$$

where again $\xi_a = -1$ and $\xi_b = 1$. Atomic functions of angular momentum $l \pm 1$, in addition to that of l , are generated by this additional gradient operator and they may contribute significantly to the magnetic dipole transition moment.

The atomic orbitals centred at a and b may also be expanded from one atomic centre to the other separated by R . These orbitals are usually the normalised Slater orbitals containing radial functions like $r_\alpha^k e^{-\xi_a r_\alpha}$ ($R = n - l - 1 = 0, 1, 2, \dots$). In our chosen coordinate frame work (figure 1), the exponential functions $e^{-\xi_b r_b}$ etc centred at b may be expanded into functions centred at a in accordance with the Barnett and Coulson expansion (Barnett and Coulson 1951). Thus

$$e^{-\xi_b r_b} = \sum_{l=0}^{\infty} (-1)^l [4\pi(2l+1)]^{1/2} Y_{l0}(\hat{r}_a) \\ \times \{(\xi_b r_<) i_{l+1}(\xi_b r_<) k_l(\xi_b r_>) + (\xi_b r_>) i_l(\xi_b r_<) k_{l-1}(\xi_b r_>)\}. \quad (22)$$

In the above expansion, $r_>$ (or $r_<$) means the larger (or smaller) of r_a and R . $k_n(\xi r)$ and $i_n(\xi r)$ ($n = l, l \pm 1$) are Bessel functions (Watson 1944) which can be expressed in terms of finite series. For interchange of a and b , an extra factor of $(-1)^l$ should be introduced on the right hand side of the expansion (22). Exponential functions like $r_b e^{-\xi_b r_b}$, $r_b^2 e^{-\xi_b r_b}$ etc may be obtained by differentiating (22) with respect to r_b and using the proper recursion relations (Watson 1944).

5. Two-centre integrals

If the electronic wavefunction is given in terms of atomic orbitals, then with the help of this translational expansion of operators and orbitals, one should in principle be able to have analytical expressions for the electronic integrals. All the two-centre integrals encountered should be of the following form:

$$\int e^{-\xi_a r_a} r_a^n Y_{lm}(\hat{r}_a) r_b^m e^{-\xi_b r_b} Y_{l'm'}(\hat{r}_b) d\tau_a, \quad (23)$$

or similar expressions by interchanging a and b . This can be integrated analytically. First, we may want to express $r_b^m e^{-\xi_b r_b} Y_{l'm'}(\hat{r}_b)$ as a product of a solid spherical harmonics $r_b^{l'} Y_{l'm'}(\hat{r}_b)$ and another function like $r_b^{m-l'} e^{-\xi_b r_b}$. These two terms may be expanded into functions centred at a as discussed in the previous section. Next, integration over $d\Omega_a$ will truncate the infinite series of expansion (as obtained from the $r_b^k e^{-\xi_b r_b}$ expansion) in l [see (22)]. The final integration is over dr_a . By expressing $k_l(\xi_b r)$ and $i_l(\xi_b r)$ in terms of finite series, the remaining radial integral breaks into a linear combination of integrals which can be integrated analytically. Thus for $l \geq 0$ and $n \geq (l+1)$; we have

$$\int_R^\infty r^n k_l(\xi_b r) e^{-\xi_a r} dr = (-1)^{l+1} \xi_b^{-1} \sum_{p=0}^l \sum_{s=0}^d \frac{(l+p)! d! R^{d-s} e^{-(\xi_a + \xi_b) R}}{2^p p! (l-p)! \xi_b^p (d-s)! (\xi_a + \xi_b)^{s+1}}, \quad (24)$$

where $d = n - 1 - p$ and

$$\begin{aligned} \int_0^R r^n i_l(\zeta_b r) e^{-\zeta_a r} dr &= (2\zeta_b)^{-1} \sum_{p=0}^l \frac{(l+p)! d!}{2^p p! (l-p)! \zeta_b^p} \\ &\times \left\{ \frac{(-1)^p}{(\zeta_a - \zeta_b)^{n-p}} + \frac{(-1)^{l+1}}{(\zeta_a + \zeta_b)^{n-p}} \right. \\ &\left. + \sum_{s=0}^d \frac{R^{d-s}}{(d-s)!} \left[\frac{(-1)^{p+1} e^{-(\zeta_a - \zeta_b)R}}{(\zeta_a - \zeta_b)^{s+1}} + \frac{(-1)^l e^{-(\zeta_a + \zeta_b)R}}{(\zeta_a + \zeta_b)^{s+1}} \right] \right\}; \\ &\zeta_a \neq \zeta_b. \end{aligned} \quad (25)$$

For the case $\zeta_a = \zeta_b$, the curly bracket on the right hand side of (25) becomes

$$\left\{ \frac{(-1)^p R^{n-p}}{d! (n-p)} + \frac{(-1)^{l+1}}{(\zeta_a + \zeta_b)^{n-p}} + \sum_{s=0}^d \frac{(-1)^l R^{d-s} e^{-(\zeta_a + \zeta_b)R}}{(d-s)! (\zeta_a + \zeta_b)^{s+1}} \right\}. \quad (26)$$

Hopefully, these sort of analytical expressions may be achieved for radiative interactions. For non-radiative interactions in diatomic molecules, one may not be sure, since the form of the integrals will depend on the choice of the interaction operators. Search for analytical expressions of two-centre integrals is an old phenomenon (Joy and Parr 1958; Prosser and Blanchard 1962; Geller 1964). In some of the methods, the operator expansion is not even necessary. But in these methods one can treat coulombic type two-centre integrals only, and furthermore these cannot treat all cases with generality. The analytical expressions achieved through translational expansion of orbitals and operators seem to be quite general for radiative interactions.

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On scattering from fractal lattices

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Abstract. Gas-surface scattering is speculated as a meaningful problem for understanding the physics of fractals. Fractal behaviour can be associated with a self-similar geometry on a solid surface. The interaction potential for a gas atom or molecule approaching the lattice depends primarily on local factors but a parametric dependence of the cross-section data on the fractal dimension can be conceived. Such a dependence on the self-similar character of a multi-centred target is more explicit when multiple scattering is included. Application of approximation schemes like the previously developed average wavefunction method to this problem is suggested.

Keywords. Fractal; scattering; gas-surface.

1. Introduction

Leo Kadanoff, in a recent article (Kadanoff 1986), wrote that ‘. . . the physics of fractals is waiting to be born’. Heterogeneous reaction dynamics is an area where the physics is expected to have a direct correlation with the fractal behaviour (Mandelbrot 1983; Pfeifer and Avnir 1983) of a surface lattice. Not surprisingly, among the first problems in chemical physics, where the relevance of fractals is seen, is that of understanding the catalytic properties of solid surfaces (Meakin 1986). The importance of gas-surface scattering in the understanding of processes occurring on surfaces is well-known (Singh and Deb 1986). A major problem that remains unresolved is the physics of scattering from disordered surfaces. The many-body and abruptly discontinuous nature of an interface presents serious difficulties. The characterization of a random system usually requires large-scale computational exercise. The fractal dimension is a possible way out (Mandelbrot 1983). We suggest here a problem based on this possibility.

A completely random fractal, e.g., the Brownian fractal fills up the space completely. The dimension of such a fractal is known to be that of the euclidean space (d) that it is embedded in. The degree of disorder in a system, say, a solid surface, can be characterized in terms of a fractal dimension (d_f) provided a self-similar behaviour is obtained at a macroscopic level. This is a feature that should be utilized to explore the physics of surface phenomena. In theoretical work involving numerical calculations, one has to work with a finite fractal. However, the dimension d_f can still be well-defined, as long as the self-similarity properties remain understood. For a gas-surface scattering problem, one can use it as a description of the relevant geometry and the interaction potential on the solid

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surface. Thus it is sensible to explore the utility of fractal dimension as a parameter describing the dynamical information inherent in, say, the angular distribution of scattering cross-section. This structure and the dynamics utility of fractal character is well-studied for the case of proteins (Colvin and Stapleton 1985; Helman *et al* 1984; Liu 1985; Wagner *et al* 1985). A detailed stochastic description of a surface that can be extrapolated to all scales has been seen to be related to the fractal dimension for ocean topography (Ausloos and Berman 1985). Montroll and Schlesinger (1983) showed the formal connection between the fractal description of dynamics and other alternatives, namely, the maximum entropy formalism and various distribution functions giving statistical descriptions.

Following a general discussion in §2, we present in §3 the application of the average wavefunction method (AWM) to the scattering from fractal lattices. A number of problems arise in the formulation even at the simplest level for a diagnostic exercise. These are discussed in §4 with brief remarks on the direction of this work.

2. The problem and the methodology

Consider a structureless particle interacting with a solid surface. The target is, by its very nature, a multi-centred one and the interaction potential between the particle and the target is represented by $V^{d_f}(\mathbf{r})$, which has the information about the geometry of the surface. In other words, it has in it the locations of all the atomic sites on the surface. Hence it is meaningful to label it with the parameter d_f . The dimension d_f can be defined in terms of an appropriate scaling property. For example, one may define d_f from $R \propto N^{1/d_f}$, where N is the number of atomic sites in a circle of radius R . Such a potential can also describe approximately, an atom interacting with adsorbate atoms on the surface. The co-ordinate $\mathbf{r}$ has all the degrees of freedom in it. Some of the degrees of freedom can be removed depending on the nature of the problem. Realistic systems like fume silica, graphite, crushed glass and colloidal systems are known to exhibit fractal behaviour (Pfeifer and Avnir 1983) and an interaction potential like the one discussed here can be used for these cases.

In any case, the scattering process is described by the following Schrödinger equation,

$$[-(\hbar^2/2m)\nabla^2 + V^{d_f}(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (1)$$

where m is the mass of the incident particle and E is its energy. The parametric dependence of the interaction potential on the fractal dimension is meaningful even if the surface lattice is not a fractal, except that then $d = d_f = d_T$ (topological dimension). The last equality may not be true for some specific models, e.g., if all the atoms are assumed to be located on a curve coiling like a wire on a surface.

Equation (1) can be written in the integral (Lippmann-Schwinger) form,

$$\psi_{\mathbf{k}}^{+d_f}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \int G_+(\mathbf{r}, \mathbf{r}') V^{d_f}(\mathbf{r}') \psi_{\mathbf{k}'}(\mathbf{r}') d\mathbf{r}', \quad (2)$$

where $\phi_{\mathbf{k}}(\mathbf{r})$ is the free-space (or appropriately distorted) plane wave with the incoming wavevector $\mathbf{k}$ (given by $\hbar^2 \mathbf{k}^2/2m = E$) and $\psi_{\mathbf{k}'}^{+d_f}(\mathbf{r}')$ is the outgoing scattered wavefunction with the wave-vector $\mathbf{k}'$. The Green's function $G_+(\mathbf{r}, \mathbf{r}')$

corresponds to the potential corresponding to $\phi_{\mathbf{k}}(\mathbf{r})$, [zero for a plane wave].

The relevant quantity of interest is the T -matrix element,

$$T^{d_f}(\mathbf{k}', \mathbf{k}) = (\phi_{\mathbf{k}'} | V | \psi_{\mathbf{k}}^{+d_f}), \quad (3)$$

and observable quantities like the differential or total cross-sections follow from the T -matrix. The central question we wish to address is whether the labelling by d_f is appropriate, i.e., whether any memory of the fractal behaviour of the lattice geometry is retained after the dynamics is over. Equation (3) shows that this should be the case though the nature of the dependence of the final results on d_f is not clear.

Thus, analysis of cross-section data from different fractal lattices can be conceived as a feasible way to explore fractal physics. A simple observation follows from (3) immediately. For a potential $V(r)$ approximated by a sum of pairwise interactions,

$$V(\mathbf{r}) = \sum_i v_i(\mathbf{r} - \mathbf{r}_i), \quad (4)$$

to retain effects arising from the geometry, one has to include multiple scattering. Thus, any approximation scheme designed to evaluate the cross-sections must take this into consideration. For instance, the first order Born approximation cannot be used for this purpose, since then the interaction in (4) gives a sum of single site scattering effects. This is not necessarily true for cases where the pairwise interaction approximation is not used. However, the analysis then becomes more involved, both conceptually and numerically.

3. Average wavefunction method

In the (AWM) approximation scheme, the atom-surface scattering is represented by a potential, which can be written as a sum of two parts. One part is a strong surface potential $V_0(\mathbf{r})$, depending only on the normal distance to surface, the second component $V_1(\mathbf{r})$ is a weaker, short-range corrugation potential that reflects the atomic structure of the topmost layer of the surface. This is taken to be of the form

$$V_1(\mathbf{r}) = \sum_i v_i(\mathbf{r} - \mathbf{r}_i), \quad (5)$$

Assuming that the dynamics due only to $V_0(\mathbf{r})$ can be solved, we have the Lippmann-Schwinger equation,

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = \chi_{\mathbf{k}}^+(\mathbf{r}) + \sum_i \int G_+(\mathbf{r}, \mathbf{r}') v_i(\mathbf{r}' - \mathbf{r}_i) \psi_{\mathbf{k}}^+(\mathbf{r}') d\mathbf{r}', \quad (6)$$

where $\chi_{\mathbf{k}}^+(\mathbf{r})$ are the scattering states of the potential $V_0(\mathbf{r})$; $G_+(\mathbf{r}, \mathbf{r}')$ is the outgoing Green's function of the Schrödinger equation with potential $V_0(\mathbf{r})$.

In the AWM scheme, one approximates $\psi_{\mathbf{k}}^+(\mathbf{r})$ as,

$$\bar{\psi}_{\mathbf{k}}(\mathbf{r}) = \chi_{\mathbf{k}}^+(\mathbf{r}) + \sum_i \lambda_i \gamma_i \int d\mathbf{r}' G_+(\mathbf{r}, \mathbf{r}') v_i(\mathbf{r}' - \mathbf{r}_i) \omega_i(\mathbf{r}'), \quad (7)$$

$$\text{where } \gamma_i = \int d\mathbf{r} \omega_i^*(\mathbf{r}) v_i(\mathbf{r} - \mathbf{r}_i) \bar{\psi}_{\mathbf{k}}(\mathbf{r}), \quad (8)$$

and $\lambda_i^{-1} = \int d\mathbf{r} |\omega_i(\mathbf{r})|^2 v_i(\mathbf{r} - \mathbf{r}_i)$, (12)

and $\omega_i(\mathbf{r})$ is a weighting factor. In the zeroth order of the approximation it is taken to be $\chi_k^+(\mathbf{r})$. The reason for this choice is explained in our earlier work (Singh *et al.* 1986a, b).

The T -matrix is obtained from

$$T(\mathbf{k}', \mathbf{k}) = T_0(\mathbf{k}', \mathbf{k}) + T_1(\mathbf{k}', \mathbf{k}), \quad (13)$$

where $T_0(\mathbf{k}', \mathbf{k}) = (\phi_{\mathbf{k}'} | V_0 | \chi_{\mathbf{k}}^+)$, (14)

and $T_1(\mathbf{k}', \mathbf{k}) = (\chi_{\mathbf{k}'} | \bar{V} | \bar{\psi}_{\mathbf{k}})$,

the potential, $\bar{V}$ represents the AWM approximated non local, separable interaction.

4. Further developments

The application of AWM to model problems (Singh *et al.* 1986b, c) has shown that it is a useful time saving approximation, at least for a better qualitative understanding of scattering from a solid surface. For this work, we have used one dimensional fractal lattices ($d_f = \log 2/\log 3$; $\log 3/\log 5$) with no background potential ($V = 0$, non-zero hard-wall like or more realistic ones being the next step). The preliminary set of calculations are being performed on a set of 16 and 18 atoms respectively with the above mentioned fractal dimensions. The T -matrix shows the following behaviour for spherically symmetric Gaussian repulsive potential at each atomic site.

$$T(\mathbf{k}', \mathbf{k}) \propto \exp(-\Delta k^2/2) \operatorname{erf}(i\Delta k/\sqrt{2}) + \sum_j \gamma_j \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_j) \quad (15)$$

where $\Delta \mathbf{k} = \mathbf{k}' - \mathbf{k}$, $\operatorname{erf}(z)$ is the error function in z , γ_j is defined in (8) and $\mathbf{r}_j$ in (9). The arguments of the first exponential and the error function in (15) are scaled appropriately with respect to the variance of the Gaussian, which is taken to be identical at each site. Even at this simple level, a number of technical as well as conceptual problems arise. First, a sizable computational facility is necessary (a lattice of N atoms requiring an inversion of a matrix of size $N \times N$ for every set of differential cross-section data). Though simplistic, these lattices are expected to show trends that can be investigated (for fractal behaviour) for larger lattices. The calculations done so far have shown distinct features in the cross section for the two different lattices. More work needs to be done, however, to reach a conclusive stage (Singh and Chattaraj 1987).

5. Conclusion

We presented in this paper a possible way to explore the relevance of fractal behaviour in scattering from solid surfaces. The average wavefunction method is chosen to ensure that multiple scattering effects are taken care of while preserving the unitarity of the Hamiltonian as well as to have analytical expressions that can be evaluated without much labour. However, even at a simple level, the calculations

are reasonably large. Still, we hope to gain some directions towards further research in understanding the physics of fractals. Increasingly more work is being done in chemical physics to explore the significance of fractal behaviour in determining the physics and chemistry of a system rather than merely measuring the dimension.

Though no rigorous analysis of how the fractal behaviour is retained in a dynamical output has been presented here, we wish to explore this in our future work. In particular, an interaction potential with an analytical fractal behaviour can be conceived (Mandelbrot-Weierstrass interaction?) and questions can be asked on what happens to this function after a non-linear transformation of the Lippmann-Schwinger kind.

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Trajectory approach to the calculation of sticking probability

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Abstract. Using a path integral approach, we propose a method for the calculation of sticking probability of atoms on solid surfaces. The method makes use of a sticking trajectory for the calculation. The formalism is illustrated by applying it to the collision of an atom with a solid, the solid being modelled as a collection of bosons, the interaction term in the Hamiltonian being linear in the boson coordinates.

Keywords. Sticking probability; trajectory approach; boson coordinates; path integral approach.

1. Introduction

Both in atomic and surface physics, some attention has been paid to methods of finding trajectories, suited for the description of specified processes. Pechukas (1969) and Pechukas and Davis (1972) have considered the problem of finding a trajectory for a particle, interacting with a quantum mechanical system, which as a result of the interaction undergoes a transition from a given initial state to a specified final state. They make use of the "path integral as a functional" approach (Feynman and Hibbs 1965) for this purpose. In surface physics, the question of finding trajectories for particles interacting with surfaces has been studied using the same technique. The infinite degrees of freedom of the solid have prompted search for an average description in which the solid's degrees of freedom have been traced out (Sebastian 1981; Mohring and Smilansky 1980; Nourtier 1985; Newns 1985). Newns (1985) advocates the opposite case of finding trajectories which are suitable for a given loss of energy and momentum. This is in the same spirit as Pechukas (1969) and Metiu and Schön (1984). For interesting related work, see Brenig (1982) and Nourtier (1985).

2. Formalism

In this paper, we consider the problem of sticking of atoms on surfaces. An approach which has been used to calculate the probability of sticking (Brako and Newns 1980; Schönhammer and Gunnarsson 1981) is to assume that the particle follows the elastic trajectory, find the spectrum of excitations produced in the solid, and calculate the sticking probability as the probability that excitations of energy greater than the initial kinetic energy of the atom are produced in the solid. This elastic trajectory approach, while justifiable when applied to inelastic scattering, is not so in the case of sticking. It also has the defect of not conserving the energy,

i.e. the energy gained by the solid is not equal to the energy lost by the atom. One possibility of improving the situation is to modify the classical equations of motion of the projectile by including the effect of energy loss to the solid. This would, however, lead to a trajectory that would either stick or not; a priori there is no way of predicting what would happen. In the following, we propose a method which overcomes these difficulties. It conserves energy and is guaranteed to stick. Our procedure is similar to the one already used by Sebastian (1981) and Mohring and Smilansky (1980, 1981). However, we do not perform a full trace over all the final states of the solid, but only over those final states that have an excitation energy greater than ε , the initial kinetic energy of the incident atom.

To keep the notation simple, we assume a one-dimensional model for both the solid and the incoming atom as done by Newns (1985). We assume the atom to be at the position Q_i at the time t_i , sufficiently far from the solid so that the interaction between the two can be neglected. At this time the solid is assumed to be in the ground state $|0\rangle$. Using quantum mechanical descriptions for both the atom and the solid, we write the probability of finding the atom at Q_f at the time t_f , given that the solid has been excited to states having excitation energy greater than ε , as the double path integral in (1),

$$P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DQ \int D\tilde{Q} \exp \left[\frac{i}{\hbar} \{S_0[Q] - S_0[\tilde{Q}]\} \right] F[Q, \tilde{Q} | \varepsilon]. \quad (1)$$

The path integration is to be carried out over all pairs of paths $Q(t)$ and $\tilde{Q}(t)$ of the atom, obeying

$$\left. \begin{aligned} Q(t_i) &= \tilde{Q}(t_i) = Q_i, \quad \text{and} \\ Q(t_f) &= \tilde{Q}(t_f) = Q_f. \end{aligned} \right\} \quad (2)$$

$$S_0[Q] = \int_{t_i}^{t_f} dt \left\{ \frac{m}{2} \dot{Q}^2 - V_0(Q) \right\}.$$

$S_0[Q]$ is the action for the atom, m the mass and $V_0(Q)$ the static part of the potential of the interaction between the atom and the solid. All the dynamical interactions are contained in the *modified influence functional*,

$$F[Q, \tilde{Q} | \varepsilon] = \langle 0 | U^+(t_f, t_i; \tilde{Q}) \hat{P}(\varepsilon) U(t_f, t_i; Q) | 0 \rangle. \quad (3)$$

$U(t_f, t_i; Q)$ is the time development operator for the solid which is under the influence of the atom, following the trajectory $Q(t)$. $\hat{P}(\varepsilon)$ is a projection operator which projects out all those states of the solid having an excitation energy greater than ε . It can be written as

$$\hat{P}(\varepsilon) = \Theta(\hat{H}_s - E_0 - \varepsilon), \quad (4)$$

where $\hat{H}_s$ is an appropriately chosen Hamiltonian for the solid (see below). $\Theta(x)$ is the step function, defined by $\Theta(x) = 1$, if $x \geq 0$, and $\Theta(x) = 0$, when $x < 0$. If we put $\varepsilon = -\infty$ then $F[Q, \tilde{Q} | \varepsilon]$ becomes identical with the influence functional used earlier (Sebastian 1981; Mohring and Smilansky 1980). $\hat{P}(\varepsilon)$ can also be written as

$$\hat{P}(\varepsilon) = \sum_{\substack{n \\ E_n - E_0 \geq \varepsilon}} |n\rangle\langle n|, \quad (5)$$

where $|n\rangle$ are eigenstates of $\hat{H}_s$ having energy E_n .

We shall take $\hat{H}_s$ as the Hamiltonian for the solid, interacting with the atom, which is kept fixed at its equilibrium adsorbed position. Defining $\Phi[Q, \tilde{Q}]$ by

$$\exp\{(i/\hbar)\Phi[Q, \tilde{Q}]\} = F[Q, \tilde{Q}|\varepsilon], \quad (6)$$

we have

$$P(Q_f, t_f; Q_i, t_i|\varepsilon) = \int DQ \int D\tilde{Q} \exp \left[\frac{i}{\hbar} \{S_0[Q] - S_0[\tilde{Q}] + \Phi[Q, \tilde{Q}]\} \right]. \quad (7)$$

We now go over to the centre of mass and relative coordinates (Schmid 1982; Newns 1985). Defining

$$\begin{aligned} R(t) &= \frac{1}{2} [Q(t) + \tilde{Q}(t)], \text{ and} \\ r(t) &= Q(t) - \tilde{Q}(t), \end{aligned} \quad (8)$$

we obtain

$$P(Q_f, t_f; Q_i, t_i|\varepsilon) = \int DR \int Dr \exp \left[\frac{i}{\hbar} \{S_0[R + \frac{r}{2}] - S_0[R - \frac{r}{2}] + \Phi[R + \frac{r}{2}, R - \frac{r}{2}]\} \right]. \quad (9)$$

Clearly

$$R(t_i) = Q_i, R(t_f) = Q_f \text{ and } r(t_i) = r(t_f) = 0. \quad (10)$$

From the definition of the functional $\Phi[Q, \tilde{Q}]$ it is easy to see that $\Phi[Q, \tilde{Q}] = -\Phi[\tilde{Q}, Q]^*$. Denoting the real and imaginary parts of $\Phi[Q, \tilde{Q}]$ by $\Pi[R, r]$ and $\Sigma[R, r]$, we see that

$$\Pi[R, r] = -\Pi[R, -r],$$

and

$$\Sigma[R, r] = \Sigma[R, -r]. \quad (11)$$

Now expanding the functionals S_0 , $\Pi[R, r]$ and $\Sigma[R, r]$ as functional Taylor series in $r(t)$, we get

$$\begin{aligned} P(Q_f, t_f; Q_i, t_i|\varepsilon) &= \int DR \int Dr \exp \left[\frac{i}{\hbar} \int_{t_i}^{t_f} dt \{m\dot{R}(t)\dot{r}(t) - V_0'(R(t))r(t)\} \right. \\ &\quad + \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t)=0} r(t) + i \Sigma[R, 0] \\ &\quad \left. + \frac{i}{2} \int_{t_i}^{t_f} dt_1 r(t_1) \left(\frac{\delta^2 \Sigma[R, r]}{\delta r(t) \delta r(t_1)} \right)_{r(t)=0} r(t) + \dots \right]. \end{aligned} \quad (12)$$

V_0' denotes the first derivative of V_0 . Note that some of the terms in the Taylor expansion vanish, due to the properties of $\Pi[R, r]$ and $\Sigma[R, r]$, given in (11). As done by earlier workers (Newns 1985; Schmid 1983), we shall neglect terms of cubical and higher order in $r(t)$ (see these papers for a discussion of the validity of this approximation). Introducing a Gaussian random function $\xi(t)$ obeying

$$\langle \xi(t) \rangle = 0 \text{ and } \langle \xi(t) \xi(s) \rangle = \frac{1}{\hbar} \left(\frac{\delta^2 \Sigma[R, r]}{\delta r(t) \delta r(s)} \right)_{r(t_i)=0}, \quad (13)$$

where $\langle \dots \rangle$ denotes averaging over the random function, we can write (12) as

$$\begin{aligned} P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DR \int Dr \left\langle \exp \left\{ \frac{i}{\hbar} \int_{t_i}^{t_f} dt \left(m\dot{R}(t)\dot{r}(t) - V_0'(R(t))r(t) \right. \right. \right. \\ \left. \left. \left. + \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t_i)=0} r(t) + r(t) \xi(t) \right) \right\} \right\rangle \exp \left(-\frac{\Sigma[R, 0]}{\hbar} \right). \end{aligned} \quad (14)$$

Now performing the path integration over $r(t)$, we obtain

$$\begin{aligned} P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DR \left\langle \delta \left[-m\ddot{R} - \frac{\partial V_0}{\partial R} + \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t_i)=0} \right. \right. \\ \left. \left. + \xi(t) \right] \right\rangle \exp \left(-\frac{\Sigma[R, 0]}{\hbar} \right). \end{aligned} \quad (15)$$

$\delta[\dots]$ stands for the delta functional. From (14), it is clear that only paths $R(t)$, obeying

$$m\ddot{R} + V_0'(R(t)) = \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t_i)=0} + \xi(t), \quad (16)$$

contribute to the probability. In order to calculate $P(Q_f, t_f; Q_i, t_i | \varepsilon)$, we have to solve (16) for each realization of the random function $\xi(t)$, use the result in (15), perform the path integral and average over $\xi(t)$. This is very tedious. So we replace $\xi(t)$ in (15) by its average value, viz zero. This means that instead of (16), we now have the equation

$$m\ddot{R} + V_0'(R) = \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t_i)=0}. \quad (17)$$

Let us denote the trajectory which obeys this equation and the boundary conditions $R(t_i) = Q_i$ and $R(t_f) = Q_f$ by $\bar{R}(t)$. In principle, there may be many trajectories obeying these conditions. In the following, we consider the case where there is only one such trajectory. Equation (15) now becomes

$$\begin{aligned} P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DR \delta \left[-m\ddot{R} - \frac{\partial V_0}{\partial R} \right. \\ \left. + \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t_i)=0} \right] \exp \left(-\frac{\Sigma[R, 0]}{\hbar} \right). \end{aligned} \quad (18)$$

The path integral in (18) can be evaluated exactly. As the evaluation is long and tedious, we just give the final result here (see Sebastian 1987, for details). It is

$$P(Q_f, t_f; Q_i, t_i | \varepsilon) = \frac{1}{2\pi\hbar} \left| \frac{\partial Q_f}{\partial P_i} \right|^{-1} \exp \left[-\int_{t_i}^{t_f} db \ddot{U}(b, b) \right] \exp \left(-\frac{\Sigma[\bar{R}, 0]}{\hbar} \right) \quad (19)$$

$\ddot{U}(b, b) = [(\partial^2 \tilde{U}(b, t))/\partial t^2]_{t=b}$ and $\tilde{U}(b, t)$ is the solution of

$$m \frac{\partial^2}{\partial t^2} \tilde{U}(b, t) + \left(\frac{\partial^2 V_0}{\partial R^2} \right)_{\bar{R}(t)} \tilde{U}(b, t) = \int_0^b ds \tilde{U}(b, s) \left(\frac{\delta^2 \Pi[R, r]}{\delta R(s) \delta r(t)} \right)_{r(t)=0, \substack{r(s)=\bar{R}(s)}}, \quad (20)$$

obeying the conditions $\tilde{U}(b, b) = 0$ and $[(\partial \tilde{U}(b, t))/\partial t]_{t=0} = 0$. P_i is the initial momentum with which the trajectory starts. If $[(\delta^2 \Pi[R, r])/\delta R(s) \delta r(t)]_{r(t)=0}$ were local or is causal (i.e. it contains either $\delta(t-s)$ or $\Theta(t-s)$) then (19) simplifies, as $\ddot{U}(b, b) = 0$.

As we had started with a state located at the point Q_i at the time t_i , the number of particles having initial momentum between P_i and $P_i + dP_i$ is $[(dP_i)/(2\pi\hbar)]$. If all these particles followed (17), then they would all be found between Q_f and $Q_f + dQ_f$ and hence $(1/2\pi\hbar) (dP_i/dQ_f)$ would be the "classical distribution". Equation (19) has a multiplicative correction factor to this as only the sticking particles would obey this equation. Hence the sticking probability is given by

$$s = \exp \left[- \int_{t_i}^{t_f} db \ddot{U}(b, b) \right] \exp \left[- \frac{\Sigma[\bar{R}, 0]}{\hbar} \right],$$

which can also be written as

$$s = \exp \left[- \int_{t_i}^{t_f} db \ddot{U}(b, b) \right] \langle 0 | U^+(t_f, t_i, \bar{R}) \hat{P}(\varepsilon) U(t_f, t_i, \bar{R}) | 0 \rangle. \quad (21)$$

Notice that $\langle 0 | U^+(t_f, t_i, \bar{R}) \hat{P}(\varepsilon) U(t_f, t_i, \bar{R}) | 0 \rangle$ is exactly the probability of creating excitations of energy greater than or equal to ε , and one would expect this to be the sticking probability from simple considerations.

Solving (17) is not as difficult as it may appear. Using (3) and (6), one can write

$$m\ddot{\bar{R}} + V'_0(\bar{R}) = -\text{Re} \left\{ \frac{\delta}{\delta r(t)} \ln \left\langle 0 \left| U^+ \left(t_f, t_i; R - \frac{r}{2} \right) \hat{P}(\varepsilon) U \left(t_f, t_i; R + \frac{r}{2} \right) \right| 0 \right\rangle \right\}, \quad (22)$$

$$m\ddot{\bar{R}} + V'_0(\bar{R}) = -\text{Re} \left\{ \frac{\langle 0 | U^+(t_f, t_i, \bar{R}) \hat{P}(\varepsilon) U(t_f, t_i, \bar{R}) H'_i[\bar{R}(t)] U(t, t_i, \bar{R}) | 0 \rangle}{\langle 0 | U^+(t_f, t_i, \bar{R}) \hat{P}(\varepsilon) U(t_f, t_i, \bar{R}) | 0 \rangle} \right\} \quad (23)$$

'Re' stands for the real part. $H_i[\bar{R}(t)]$ is the Hamiltonian for the time development of the solid, when the atom follows a trajectory $\bar{R}(t)$. A nice property of $\bar{R}(t)$, viz energy conservation, is easily illustrated using the above equation. For this we multiply (23) by $\dot{\bar{R}}(t) = [\partial \bar{R}(t)/\partial t]$ and integrate from t_i to t_f . This leads to

$$\begin{aligned} \left[\frac{1}{2} m \dot{\bar{R}}^2 + V_0(\bar{R}) \right]_{t=t_i} &= \left[\frac{1}{2} m \dot{\bar{R}}^2 + V_0(\bar{R}) \right]_{t=t_f} \\ &+ \text{Re} \left\{ \frac{\langle 0 | U^+(t_f, t_i, \bar{R}) \hat{P}(\varepsilon) H_i(Q_f) U(t_f, t_i, \bar{R}) | 0 \rangle}{\langle 0 | U^+(t_f, t_i, \bar{R}) \hat{P}(\varepsilon) U(t_f, t_i, \bar{R}) | 0 \rangle} \right\} \end{aligned} \quad (24)$$

which shows that the particle loses exactly the same energy as the energy gained by the solid due to all excitations having energy greater than ϵ .

To solve (23), one can start with the particle at Q_i at the time t_i and take the initial momentum to be P_i . Using these two inputs and neglecting the term on the left hand side, one can calculate the elastic trajectory $\bar{R}_{el}(t)$. This may be used on the left hand side of (23), as an approximation to $\bar{R}(t)$ and the equation solved again, to find a better approximation for $\bar{R}_{el}(t)$. This procedure may be continued until convergence is attained. However, choosing values for t_f and Q_f can be a problem. It appears to be reasonable to take Q_f to be the equilibrium position of the atom and t_f to be the time when the particle has hit the solid and has executed a few oscillations near it. One also expects the sticking probability to be independent of the values of Q_f and t_f so chosen. Numerical calculations are being planned and will be reported later.

3. Application to a simple Hamiltonian

As an illustration, we derive the equation for the sticking trajectory for the case of an atom interacting with the phonons of the solid, with the total Hamiltonian given by

$$\hat{H}_s = \sum_k \hbar \omega_k b_k^+ b_k + \sum_k F(k, Q) (b_k^+ + b_k) + \frac{p^2}{2m} + V_0(Q). \quad (25)$$

$p^2/2m$ is the kinetic energy of the atom and $V_0(Q)$ is the static part of the interaction between the atom and the solid. That is, it represents the interaction between the atom and the solid, when all the solid atoms occupy their equilibrium positions. $\sum_k \hbar \omega_k b_k^+ b_k$ is the phonon Hamiltonian, and the last term in the Hamiltonian represents the interaction between the phonons and the atom. This Hamiltonian has been considered by many authors (Kaplan and Dragulis 1967; Brako and Newns 1982; Newns 1985). One can take Q_f to be Q_e , where Q_e is the minimum of the potential $V_0(Q)$. Let us take $\hat{H}_s$ to be the Hamiltonian for the solid with the atom kept fixed at Q_e , i.e.

$$\hat{H}_s = \sum_k \hbar \omega_k b_k^+ b_k + \sum_k F(k, Q_e) (b_k^+ + b_k). \quad (26)$$

We take $|n\rangle_s$ in (5) to be eigenfunctions of this Hamiltonian.

Equation (22) now becomes

$$m\ddot{\bar{R}} + V'_0(\bar{R}) = -\text{Re} \sum_k \frac{\langle 0 | U^+(t_f, t_i; \bar{R}) \hat{P}(\epsilon) U(t_f, t; R) (b_k^+ + b_k) U(t, t_i; \bar{R}) | 0 \rangle F'(k, \bar{R})}{\langle 0 | U^+(t_f, t_i; \bar{R}) \hat{P}(\epsilon) U(t_f, t_i; \bar{R}) | 0 \rangle}, \quad (27)$$

$F'(k, \bar{R}) = [\partial F(k, R)/\partial R]_{R=\bar{R}(t)}$. In the last term of (27), using the commutation relations of b_k and b_k^+ , one can move b_k to the right hand extreme so that it annihilates $|0\rangle$, and similarly, b_k^+ to the left hand extreme. b_k^+ , however, has to be moved across $\hat{P}(\epsilon)$ for which one can make use of the following identity:

$$\dot{P}(\varepsilon) b_k^+ = b_k^+ \dot{P}(\varepsilon - \omega_k) + \frac{F(k, Q_c)}{\hbar \omega_k} \{ \dot{P}(\varepsilon - \hbar \omega_k) - \dot{P}(\varepsilon) \}. \quad (28)$$

This can be easily obtained from the definition of $\dot{P}(\varepsilon)$. Equation (27) can now be written as

$$\begin{aligned} m\ddot{\bar{R}} + V'_0(\bar{R}) &= \frac{1}{\hbar} \sum_k F'(k, \bar{R}) \int_{t_i}^{t_f} dt_1 F(k, \bar{R}) \sin \omega_k |t - t_1| \\ &- \sum_k \frac{F'(k, \bar{R}) F(k, \bar{R})}{\hbar \omega_k} \cos \omega_k (t_f - t) \left\{ \frac{\langle\langle \dot{P}(\varepsilon - \omega_k) \rangle\rangle}{\langle\langle \dot{P}(\varepsilon) \rangle\rangle} - 1 \right\} \\ &- \frac{1}{\hbar} \sum_k \frac{F'(k, \bar{R})}{\langle\langle \dot{P}(\varepsilon) \rangle\rangle} \langle\langle \dot{P}(\varepsilon - \omega_k) \rangle\rangle \int_{t_i}^{t_f} dt_1 F(k, \bar{R}) \sin \omega_k (t - t_1), \quad (29) \\ &= \frac{1}{\hbar} \sum_k F'(k, \bar{R}) \int_{t_i}^{t_f} dt_1 F(k, \bar{R}(t_1)) \sin \omega_k (t - t_1) \\ &\quad \left\{ \operatorname{sgn}(t - t_1) - \frac{\langle\langle \dot{P}(\varepsilon - \omega_k) \rangle\rangle}{\langle\langle \dot{P}(\varepsilon) \rangle\rangle} \right\} \\ &- \sum_k \frac{F'(k, \bar{R}) F(k, \bar{R}_c)}{\hbar \omega_k} \cos \omega_k (t_f - t) \left\{ \frac{\langle\langle \dot{P}(\varepsilon - \omega_k) \rangle\rangle}{\langle\langle \dot{P}(\varepsilon) \rangle\rangle} - 1 \right\}. \quad (30) \end{aligned}$$

This equation, though it looks complicated, can be applied to the problem of sticking as outlined here: (i) start with the elastic trajectory $\bar{R}_{el}(t)$ as an approximation, (ii) evaluate $\langle\langle \dot{P}(t) \rangle\rangle$ with this, use them to calculate the right hand side of (30), solve this equation to get a better approximation to $\bar{R}(t)$ and continue this until self-consistency is achieved. Calculating $\langle\langle \dot{P}(\varepsilon) \rangle\rangle$ can be done easily as we now have a system of forced harmonic oscillators, for which the explicit formula is given by Muller-Hartman *et al* (1970).

Acknowledgement

This work was supported by a research grant from the Kerala State Committee on Science, Technology and Environment.

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On the development of many-body theories for intramolecular dynamics

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Abstract. The efficacy of using time-dependent generalizations of the closed shell coupled cluster method for intramolecular processes associated with non-degenerate vacuum in the context of molecular absorption spectra is examined. Since the separability requirements are built into such an ansatz for the time evolution operator, it is possible to develop approximations which can take into account any number of modes, with much less computational effort than in a calculation by basis set expansion.

Keywords. Coupled cluster method; intramolecular dynamics; time-dependent generalizations.

1. Introduction

The calculation of molecular optical processes in large anharmonic molecules is one of the fundamental problems in molecular spectroscopy. Recent experimental studies on ultra-cold molecules in supersonic beams are yielding accurate information (Smalley 1982, 1983; Levy 1980, 1981), and these in turn have spurred a large number of theoretical studies on this subject (e.g. Heller 1981a, Mukamel 1985).

The analysis of spectra of isolated molecules is traditionally made in terms of molecular vibronic eigenstates (Herzberg 1966). For example, the expression for the molecular absorption spectra reads

$$P(\omega) = \sum |\langle \psi_n | \mu | \psi_g \rangle|^2 \delta(\epsilon_n - \epsilon_0 - \omega). \quad (1)$$

Here $P(\omega)$ is the intensity, ψ_n and ϵ_n are the vibronic states of the upper electronic states and their energies, ψ_g is the ground state of the lower surface and μ is the dipole operator. Calculation of absorption spectrum from (1) requires an accurate knowledge of ψ_n and ϵ_n . For small molecules it is possible to diagonalize the vibrational part of the Hamiltonian on the excited state surface. However, such a procedure is impractical for intermediate to large molecules. In order to overcome this problem, methods based on the correlation functions were developed to calculate the molecular spectra (Mukamel 1982a, b, 1984, 1985; Heller 1981a, b; Reimers *et al* 1983; Coalson and Karplus 1982, 1983; Noid *et al* 1981; Islampour and Mukamel 1984a, b; Berne and Harp 1970; Gordon 1968). Within the framework of Born-Oppenheimer approximation, and assuming that the dipole operator depends

only weakly on the nuclear coordinates, (1) may be rewritten for a single excited electronic state in the form of an autocorrelation function as follows:

$$P(\omega) = \mu_{eg} \int_{-\infty}^{\infty} \langle \phi_g(0) | \phi_g(t) \rangle \exp(i\omega t) dt. \quad (2)$$

Here, μ_{eg} is the matrix element of the dipole operator between the ground and excited electronic states, ϕ_g is the vibrational ground state of the lower surface, and,

$$|\phi_g(t)\rangle = \exp(-iH_u t) |\phi_g(0)\rangle, \quad (3)$$

where H_u is the vibrational Hamiltonian of the upper surface.

Several approximations, based upon classical and semiclassical mechanics have been developed to calculate the auto-correlation functions for large systems and tested on a few model systems (Heller 1981b; Mukamel 1982a; Warshel *et al* 1983).

In the present communication we develop a fully quantum-mechanical theory for the description of intramolecular dynamics and the calculation of auto-correlation functions based on the time-dependent coupled cluster method. Since the separability requirements of many particle systems are built into any ansatz based on the coupled cluster method, it is possible to develop approximations to the time evolution operator (and thus to the correlation functions) which can take into account any number of modes with much less computational effort than in a calculation by basis set expansion. Section 2 contains the theoretical development of our work and §3 the concluding remarks.

2. Theory

The molecular vibrational Hamiltonians are given in normally ordered form, as

$$H(\alpha) = \sum \omega_{ij}(\alpha) a_i^\dagger a_j + \sum V_{mn}^{ij}(\alpha) (a_i^\dagger)^m (a_j)^n + \dots \quad (4)$$

Here α is the index of the electronic state, $a_i^\dagger$, a_i are the usual creation and annihilation operators of the i th mode, ω_{ij} are the frequencies, and V_{mn}^{ij} etc. are the various anharmonic coupling constants. We define the origin of the molecule fixed coordinate frame at the minimum of the ground electronic surface and expand the potential energy $V(\alpha)$ in terms of the normal coordinates of that state. Since the anharmonicity terms rarely affect the vibrationless state to any appreciable extent, we can approximate the doorway state $|\phi_g\rangle$ as

$$|\phi_g\rangle = |0\rangle, \quad (5)$$

where $|0\rangle$ is the vacuum state for the operators a_i .

The time development of the vacuum state is given by the coupled cluster ansatz in a normal ordered form as

$$\begin{aligned} |t\rangle &= \exp(-iH_u t) |0\rangle \\ &= \exp(S) |0\rangle, \end{aligned} \quad (6)$$

where,

$$S = S_0 + S_1 + S_2 \dots, \quad (7a)$$

$$S_1 = \sum_i s_i^\dagger a_i^\dagger, \quad (7b)$$

$$S_2 = \sum_{ij} s_{ij}^2 a_i^+ a_j^+, \quad (7c)$$

$$S_3 = \sum_{ijk} s_{ijk}^3 a_i^+ a_j^+ a_k^+. \quad (7d)$$

and S_0 is a complex scalar.

The equations for the cluster amplitudes s^n are obtained from the time-dependent Schrödinger equation. In atomic units

$$i \frac{\partial}{\partial t} |t\rangle = H_u |t\rangle. \quad (8)$$

Substituting (6) into (8), premultiplying by $\exp(-S)$ and projecting onto different excited states $|m\rangle$ we obtain,

$$i\dot{s}_m = \langle m | \bar{H}_u | 0 \rangle. \quad (9)$$

Here,

$$\bar{H}_u = \exp(-S) H_u \exp(S). \quad (10)$$

Equations (10) and (11) are the working equations in the present theory. In general the expressions for $\bar{H}_u$ are non-linear in the amplitudes s_m and have to be numerically integrated, subject to the initial value conditions,

$$s_m(0) = 0. \quad (11)$$

This is required since in the doorway state picture excitation to the upper surface occurs at $t = 0$.

The auto-correlation function is given by

$$\langle t | 0 \rangle = \exp(S_0) \quad (12)$$

where S_0 is given by

$$i\dot{S}_0 = \langle 0 | \bar{H}_u | 0 \rangle. \quad (13)$$

Using (12) spectral bands of any surface can be calculated via (2).

Since the working equations (9) give full information regarding the time evolution operator, they can be used for the description of intramolecular dynamics. For example, the energy in the i th mode E_i , at any time t , is given by

$$\begin{aligned} E_i(t) &= \omega_i \frac{\langle 0 | \exp(S^+) a_i^+ a_i \exp(S) | 0 \rangle}{\langle 0 | \exp(S^+) \exp(S) | 0 \rangle} \\ &= \omega_i \langle 0 | \exp(S^+) a_i^+ a_i \exp(S) | 0 \rangle_{\text{linked}}. \end{aligned} \quad (14)$$

Here the last line follows from the linked cluster theorem of exponential ansatz (Pal *et al* 1982).

3. Concluding remarks

The main problem in a conventional approach to the calculation of optical spectra of large molecules is the dimensions of the matrices to be constructed and

diagonalized. This has led to the development of time-dependent approaches. As Heller (1981a) observed, for a frequency resolution of a few tens of wave numbers, the correlation function needs to be evaluated for a few picoseconds only. Thus the spectral band calculation reduces to the analysis of short-time intramolecular dynamics.

The present work was concerned with the development of the time-dependent coupled cluster method for the description of intramolecular dynamics. There are several advantages in the present approach. First, since the cluster amplitudes are continuous complex variables, this approach may be viewed as a quantum trajectory method, and thus, does not suffer from the limitations of the conventional basis set expansion methods. We recall, in this context, that a displaced harmonic oscillator function is represented as

$$\begin{aligned} |\phi_d\rangle &= \exp(da^+ - d^*a)|0\rangle \\ &= \exp\left(da^+ + \frac{dd^*}{2}\right)|0\rangle. \end{aligned} \quad (15)$$

Thus in the approximation $S = S_0 + S_1$, the ansatz (6) is just a travelling Gaussian function. It can be shown in a similar fashion that inclusion of S_2 takes into account, the changes in the effective force constants and frequencies. For general harmonic surfaces, (9) and (10) form a closed set with $S = S_0 + S_1 + S_2$, a feature they share with the semiclassical theories (Heller 1981a; Mukamel 1982a).

Being a fully quantum mechanical theory, the present approach has no problems in the calculation of the phase accumulated during the propagation (which is absorbed into S_0) nor does it need any additional corrections such as uniformization in the case of degeneracies. Because of these features, it is superior to the semiclassical theories. Also it does not require the calculation of overlap function $\langle t|0\rangle$ at each instant, as required in the Frozen Gaussian approach, of Heller (1981b), which is a considerable saving computationally.

In the present form, the time-dependent coupled cluster theory is limited to the dynamics of a vacuum state. Extensions to higher states are necessary before it can be applied to general intramolecular processes. Work is in progress in this direction, and shall be reported in due course.

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How can density functional theory be excited from the ground state?

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Abstract. Density functional theory (DFT) has not been applied on a large scale to time-dependent problems and problems involving excited states. Atomic and molecular collisions involving both these types of phenomena remain outside the purview of DFT. An amalgamation of quantum fluid dynamics (QFD) with DFT considerably broadens the range of applicability of traditional (ground-state) DFT. Ion-atom collisions have been studied by jointly using DFT and QFD.

Keywords. Density functional theory; quantum fluid dynamics; time-dependent phenomena; excited states; ion-atom collisions; molecular reaction dynamics.

1. Introduction

Density-based studies of many-electron systems have become popular in the last two decades due to their mathematical, physical, computational and conceptual simplicity. Two important approaches, where density is used as the basic variable instead of the many-particle wavefunction, are density functional theory (DFT) and quantum fluid dynamics (QFD) (Bamzai and Deb 1981; Ghosh and Deb 1982). The backbone of DFT is the Hohenberg-Kohn theorem (Hohenberg and Kohn 1964) which states that the ground-state energy is a unique functional of density and attains its minimum for the true ground-state density, thus providing a method for variational optimization of any arbitrary energy functional to calculate the appropriate density and energy. On the other hand, a set of two coupled equations, viz. an equation of continuity and an equation of motion (EOM), forms the basis of QFD (Deb and Ghosh 1987). By solving these two equations, one obtains the time-evolution of charge density and current density, the two basic variables in QFD. The major difference between these two approaches is that DFT cannot be applied to general dynamical situations unless the validity of a time-dependent DFT (TDDFT) is proved rigorously. In this paper we discuss the current status of DFT, emphasizing its two major drawbacks and briefly outline an approach towards their solution.

2. Two major problems of present-day DFT

Although the exact form of the energy functional is not known, due to the unknown nature of the kinetic energy (Chattaraj and Deb 1984) and exchange-correlation energy functionals, the existence of the total energy functional is guaranteed for the

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ground-state (Hohenberg and Kohn 1964). However, the number of attempts to apply DFT in time-dependent situations is relatively very small. Also, there has been no DFT calculation for obtaining the energy of an excited state. The present status concerning these two problems is reviewed below.

2.1 *Time-dependent situations*

The invertibility of the map between the TD potential and TD density should be established if one wishes to have a TD version of the Hohenberg-Kohn theorem. For a very restricted case, this was first proved by Peuckert (1978). He considered the Taylor expansion of the TD potential in the neighbourhood of zero. In a more general situation, Deb and Ghosh (1982), and subsequently Bartolotti (1981, 1982), developed a TD Kohn-Sham (TDKS) equation (Kohn and Sham 1965) to obtain the time-evolved density only in the case of a limited class of external potentials, viz. TD harmonic potentials, which do not allow any excitation. But this still leaves most TD problems outside the purview of DFT. The most general proof till today has been provided by Runge and Gross (1984), although the proof is valid only under certain conditions regarding the initial density and the time-evolution of the potential. The Runge-Gross proof has been criticised by Xu and Rajagopal (1985), according to whom this proof cannot be extrapolated to a uniform system under TD perturbation. However, an invertible mapping does exist between the TD potential and the TD current density (rather than the charge density). Nevertheless, the Runge-Gross proof does remain valid provided the TD potentials are well-behaved at large distances (Dhara and Ghosh 1987). Kohl and Dreizler (1988) have extended the Runge-Gross proof through the construction of a Levy-Lieb type functional (Levy 1979; Lieb 1983) while the extension to TD ensembles was done by Li and others (Li and Tong 1985; Li and Li 1985).

2.2 *Excited states*

Till today, DFT has been essentially a static ground-state theory. Its impressive success prompted many workers to extend DFT to excited states as well. Slater's (1974) transition state theory may be regarded as the first attempt to obtain a DFT for excited states. The subspace theory for excited states (Theophilou 1979, 1980) may be regarded as a rigorous justification of Slater's approach. It states that the composite energy quantity is a unique functional of the composite density. Katriel (1980) has interpreted Theophilou's approach as a special case of the original Hohenberg-Kohn theorem for an appropriately defined composite super-Hamiltonian. The Hohenberg-Kohn theorem has also been shown to be valid for an excited state that corresponds to the lowest state of a given symmetry (Gunnarsson and Lundqvist 1976). However, Kohn and Vashishta (1983) feel that the corresponding self-consistent equations generally do not exist. A one-to-one correspondence had also been established (Mikolas and Tomasek 1977) between the total energy of a particular state (ground or excited) and the density of the same state. Since the ground-state density fixes the Hamiltonian to within an additive constant, all the excited states of a system under a local external one-body potential would be characterized by the ground-state density. The Levy-Lieb functional (Levy 1979; Lieb 1983) encompasses a large class of excited states and provides a mathematical basis for Theophilou's idea (Hadjisavvas and Theophilou 1985). U

of single excited-state functionals, contrary to subspace functionals, has been introduced by Valone and Capitani (1981). The Hohenberg-Kohn theorem has also been extended to excited states (Hunter 1986) through the derivation of a Schrödinger-type equation satisfied by the square-root of the electron density. This may be regarded as an extension of a similar equation for the ground-state density (Deb and Ghosh 1983).

3. Broadening of DFT through QFD

There is a formal equivalence between DFT and QFD in 3-D space (Deb and Ghosh 1982). Since time occurs naturally in QFD, and a nonzero current density is obtained for most of the excited states by solving QFD EOMS, through QFD DFT can go into both TD situations and excited states. We have proposed (Deb and Chattaraj 1987) an amalgamation of QFD and DFT to give rise to quantum fluid density functional theory (QFDFT). The above two problems had prevented one from applying DFT on a large scale to the important area of molecular reaction dynamics. Since in atomic and molecular collisions both of the above problems, viz. TD situations and excited states, are involved, QFDFT has been applied (Deb and Chattaraj 1987) to deal with the high-energy proton-neon collision problem. Earlier, TD Thomas-Fermi theory and its variants were employed (Ludde *et al* 1979; Horbatsch and Dreizler 1981, 1982; Malzacher and Dreizler 1982; Horbatsch 1983) to study high-energy ion-atom collisions. Several nonlinear features were revealed through a numerical solution of two fluid dynamical equations. In the case of proton-argon collisions it was observed that the perturbation caused by the incoming proton to the target density is reflected through nonlinear oscillations of the latter. The oscillations dampen gradually with a different frequency for the inner and outer parts of the density. The present QFDFT method (Deb and Chattaraj 1987) can be considered as a generalization of these previous works. Considering the current status of TDDFT and excited state DFT it is quite reasonable to assume that the QFDFT approach is likely to be more promising than DFT itself. We have derived a TDKS equation in 3-D space which is a new nonlinear Schrödinger equation, by using a QFDFT approach as well as a stochastic interpretation of quantum mechanics (Nelson 1985). It has been argued that for any given Hamiltonian H and initial wavefunction $\psi(\mathbf{r}, t_0)$ there corresponds an equivalent Markov process in coordinate space such that the probability density $\rho(\mathbf{r}, t)$ of the particle (undergoing Brownian motion) being at $\mathbf{r}$ at the instant t coincides with that given by quantum mechanics, i.e. $|\psi(\mathbf{r}, t)|^2$ (Nassar 1984). This stochastic viewpoint further strengthens the use of QFD along with conventional DFT. A space-time-dependent "local molecular thermodynamics" has also been developed. This is an extension of the work of Ghosh *et al* (1984). The time-evolution of local "thermodynamic" variables can be obtained through the TDKS equation which has the following form (in atomic units):

$$i \frac{\partial \phi(\mathbf{r}, t)}{\partial t} + \frac{1}{2} \nabla^2 \phi(\mathbf{r}, t) + V_{\text{eff}}(\mathbf{r}, t) \phi(\mathbf{r}, t) = 0, \quad (1)$$

where

$$V_{\text{eff}}(\mathbf{r}, t) = -\frac{5}{3} C_k \rho^{2/3} + \frac{4}{3} C_x \rho^{1/3} + \frac{a(N)}{r^2} + \frac{Q}{r} + \frac{1}{|\mathbf{R} - \mathbf{r}|} - \frac{f(\mathbf{R}, N)}{N} \quad (2)$$

$$\rho(\mathbf{r}, t) = |\phi(\mathbf{r}, t)|^2. \quad (3)$$

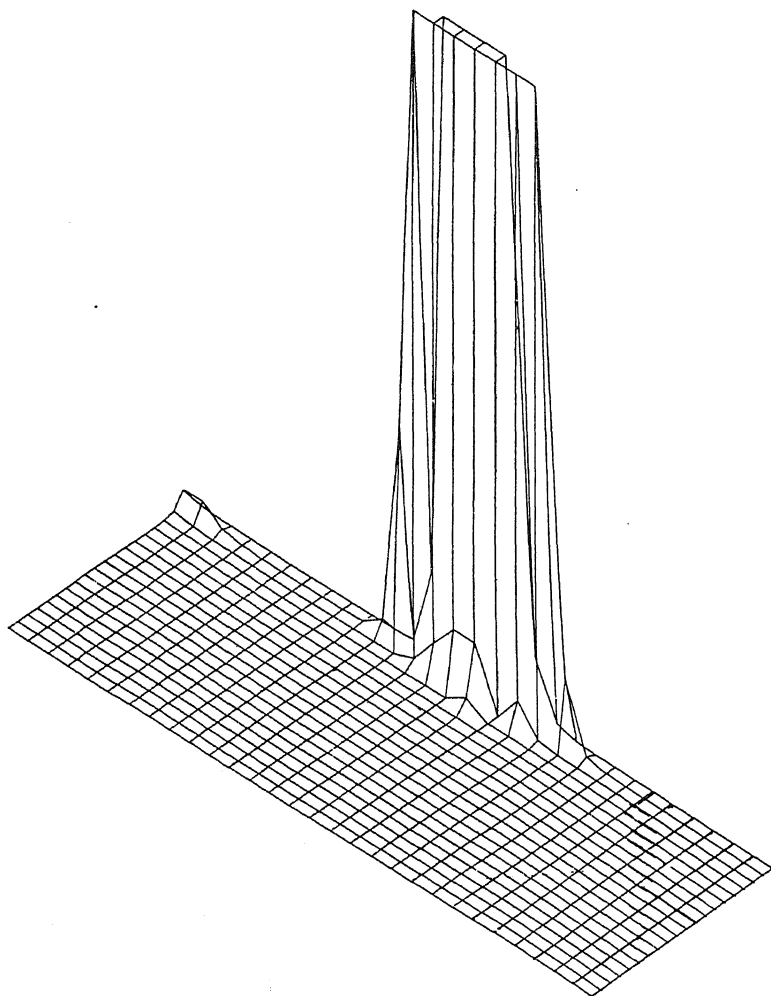


Figure 1. Perspective plot of the current density in the proton-neon colliding system, in cylindrical polar coordinates $(\bar{\rho}, z)$ at $t = 0.08$ a.u. The basal rectangular mesh designates the $(\bar{\rho}, z)$ plane, where $0 \leq \bar{\rho} \leq 3.25$ and $-3 \leq z \leq +3$; the topmost line of the basal mesh corresponds to the z axis. The target neon nucleus is at $(0, 0)$, i.e., at the mid-point of the topmost line in the basal mesh, and the proton is approaching from the left along this line (internuclear distance = 9.92 a.u.). The top cut-off value is 50.0 a.u.

Here C_k and C_x are the familiar Thomas-Fermi and Dirac constants, respectively, $a(N)$ depends on N (the total number of electrons), $f(R, N)$ is a function depending on both R and N , R being the internuclear distance; Q refers to a screened nuclear charge. The nonlinearity in (1) enters through the single-particle nonlocal potential V_{eff} , via nonintegral powers of ϕ as well as an integral occurring in Q . The high degree of nonlinearity in (1) causes serious problems in its solution.

However, in order to study high-energy proton-neon collisions, we have solved (1) numerically. Several nonlinear features reveal themselves. In particular, the possibility of solitary wave solutions is indicated; this requires further analysis. The time-dependent current density at $t = 0.08$ a.u. has been depicted in figure 1. The fact that we now come across a nonzero current density implies that, due to the approach of the proton, excited states of the neon atom are mixing with its groundstate. Due to space limitations, we refrain from giving details of this work (Deb and Chattaraj 1987). We believe that this approach has the potential to monitor a time-dependent process from start to finish.

Acknowledgement

The authors would like to thank the Council of Scientific and Industrial Research, New Delhi, for financial support.

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The iterative hole-particle method for excited states calculation: Application to tetratomic thiocarbonyls

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Abstract. The single configuration SCF calculation for excited states is proposed for the various differently optimized excited states. Different sets of occupied and unoccupied one-electron orbitals are obtained for the different excited states. Morokuma's model is extended to a semiempirical CNDO basis. The method predicts excited state geometry quite well. Qualitative agreement in the calculated transition energies, singlet-triplet splitting and barrier to inversion has been found and the results indicate no major deviation in the trends followed in similar non-iterative simple hole-potential calculation. As expected, convergence could not be achieved in all $^1\pi\pi^*$ calculations in the non-planar geometry. Calculations in the planar geometry, however, showed convergence with difficulty. One interesting feature is a gradual decrease in the energy difference between $^3n\pi^*$ and $^3\pi\pi^*$ states with successive fluorine substitution, ultimately leading to an inversion in the order in F_2CS . The prediction of $^3\pi\pi^*$ as the T_1 state in F_2CS is discussed in the context of photochemistry exhibited by certain aromatic carbonyl compounds. Probable extension of the present model to develop an average Fock operator for single excitations and also a one-electron operator for double excitations is proposed.

Keywords. Iterative hole-particle method; excited states calculation; tetratomic thiocarbonyls; singlet-triplet splitting.

1. Introduction

Features of molecular excited states can be explored rather satisfactorily in terms of single configuration (open shell) wavefunction (Roothaan 1960; Hunt and Goddard 1969). One-electron orbitals coming out from such open-shell Hartree Fock (HF) calculations are much superior to the usual ground state orbitals in giving the more correct CI expansion to the excited state wavefunction for which the open-shell single determinant serves as the reference configuration (Peyerimhoff and Buenker 1975). The V_{N-1} potential model, also referred to as the hole-potential model (HPM), provides one such means of describing the singly excited state (Huzinaga and Arnau 1970, 1971). Through a modification of only the HF virtual orbitals in the HPM, a considerable gain has been achieved in geometry, charge distribution, and transition energy of the singly excited states. This has been evident from earlier studies on the $^{1,3}n\pi^*$ and $^{1,3}\pi\pi^*$ states of some tetra-atomic thiocarbonyls (Banerjee and Bhattacharyya 1980, 1983). In an extended HF theory for excited states (Morokuma and Iwata 1972) some deficiency in the HPM theory was overcome to a great extent. The deficiency lies in the fact that the HPM theory allows a mixing among the virtual orbitals only and the 'occupied' subspace is

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projected out unchanged. This model does not consider reorganization of the occupied or 'hole' orbitals under the influence of the excited electron. In the method of Morokuma and Iwata (1972) a further degree of freedom is added in which orbital reorganization is allowed within both the intraoccupied and intravirtual manifolds through a constrained variational minimization of the total electronic energy of the excited configuration. The 'hole' orbitals undergo reorganization under the influence of the excited electron in just the same way as the 'particle' orbitals are reorganized by the hole created in the occupied manifold. A convenient name for this method may be hole-particle potential model (HPPM). In actual computation this is achieved through the iterative SCF procedure. We perform the calculation with CNDO/2 formulation of the resulting LCAO-MO SCF equation, employing only a valence AO basis set which is characteristic of such formulation. Use of a more extensive basis set would improve the results by giving more variational freedom to the orbitals.

One disadvantage of the HPPM theory stems from the fact that other configurations constructed from the optimized orbitals corresponding to a particular excited state are not optimized. Again the differently (singly excited) optimized configurations are not strictly orthogonal. In this situation one usually thinks in terms of an average Fock operator. We indicate the possibility of formulating such an operator, but in the present work we prefer to stick to the simple HPPM.

2. Theory

Let us partition the total space spanned by the closed-shell HF orbitals $\{\phi_i\}$ into two subspaces A and B which, for the present, represent the occupied and virtual manifolds respectively. We now define the Hermitian operator

$$V = \sum_{kl}^A a_{kl} |\phi_k\rangle \langle \phi_l| + \sum_{rs}^B b_{rs} |\phi_r\rangle \langle \phi_s| = V_2 + V_1, \quad (1)$$

where the numbers a_{kl} and b_{rs} constitute Hermitian matrices. It is obvious that

$$V|\phi_i\rangle = \sum_k^A a_{ki} |\phi_k\rangle = \psi_i, \quad \text{for } i \in A, \quad (2a)$$

$$V|\phi_m\rangle = \sum_r^B b_{rm} |\phi_r\rangle = \psi_m, \quad \text{for } m \in B. \quad (2b)$$

Equations (2) bring about intra- A space and intra- B space mixing. The quantities a_{ki} and b_{rm} may be chosen as matrix elements of the Hermitian operators Ω_2 and Ω_1 on the subspaces A and B , respectively, where such operators may be assumed with a certain degree of arbitrariness. If we assume the particular choice of $\Omega_{1\alpha}$ and $\Omega_{2\mu}$ and the subspace projection operators P_A and P_B are defined in terms of the Hartree Fock MO $\{\phi_i\}$ so that

$$P_A = \sum_k |\phi_k\rangle \langle \phi_k|, \quad (3)$$

(1) can be expressed as

$$V = P_A^\dagger \Omega_{2\mu} P_A + P_B^\dagger \Omega_{1\alpha} P_B. \quad (4)$$

In view of formulating singlet or triplet excited states arising out of the singly excited configuration alone, we make the following choices:

$$\begin{aligned} \Omega_{1\alpha} &= a_1 J_\alpha + b_1 K_\alpha, \\ \Omega_{2\mu} &= a_2 J_\mu + b_2 K_\mu, \end{aligned} \quad (5)$$

where for the triplet

$$a_1 = -1, \quad b_1 = 0, \quad a_2 = 1, \quad b_2 = 0$$

and for the singlet

$$a_1 = -1, \quad b_1 = 2, \quad a_2 = 1, \quad b_2 = -2. \quad (6)$$

Such ground and excited state wavefunctions are represented by the usual normalized determinantal functions

$$\Psi_0 = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \dots \phi_N \bar{\phi}_N|, \quad (7a)$$

$$\text{and } {}^{1,3}\Psi_{(\alpha \rightarrow \mu)} = |\psi_1 \bar{\psi}_1 \dots \frac{1}{\sqrt{2}} (\psi_\alpha \bar{\psi}_\mu \mp \bar{\psi}_\alpha \psi_\mu) \dots \psi_N \bar{\psi}_N|. \quad (7b)$$

Here $\{\psi_i\}$ are the new orbitals appropriate to the excited state configuration. If instead of (7b) one writes the configuration

$${}^{1,3}\Psi_{(\alpha \rightarrow \mu)} = |\phi_1 \bar{\phi}_1 \phi_2 \dots \frac{1}{\sqrt{2}} (\phi_\alpha \bar{\psi}_\mu \mp \bar{\phi}_\alpha \psi_\mu) \dots \phi_N \bar{\phi}_N|,$$

where ψ_μ is some modified upper orbital which can be obtained by a unitary mixing of the HF orbitals $\{\phi_B\}$, then one can readily write the energy expression as (Roothaan 1951)

$${}^{1,3}E = E_0 + \langle \psi_\mu | F | \psi_\mu \rangle - \langle \phi_\alpha | F | \phi_\alpha \rangle + (-J_{\alpha\mu} + K_{\alpha\mu} \pm K_{\alpha\mu}). \quad (8)$$

Variational minimization of (8) with respect to the expansion coefficients of ψ_μ leads to a one-electron equation described by the operator

$$F^b = F + P_B^\dagger \Omega_{1\alpha} P_B = F + V_1. \quad (9)$$

In (9) the projector P_B is added to ensure no mixing with A -space orbitals. This follows from the situation when $a_{kl} = 0$ for all $k, l \in A$ in the potential V of (1). Obviously, the A -space orbitals are directly eigenfunctions of F^b , but the B -space functions are not. The present situation produces the HPM theory. Similarly, the operator

$$F^a = F + P_A^\dagger \Omega_{2\mu} P_A = F + V_2, \quad (10)$$

generates modified 'hole' orbitals as eigenfunctions, but the B -space orbitals are directly eigenfunctions to it. This emerges from $b_{rs} = 0$ for all $r, s \in B$. Now, a variational minimization of the energy expression, corresponding to the configuration mentioned in (7b), generates the one-electron equations,

$$F' \psi_i = \lambda_i \psi_i,$$

$$\text{where } F' = F + P_B^\dagger \Omega_{1\alpha} P_B + P_A^\dagger \Omega_{2\mu} P_A = F + V_1 + V_2. \quad (11)$$

The entire eigenspectrum of F' contains 'new' orbitals which consider electron reorganization in both subspaces A and B in the excited state. Using the AO basis set $\{\chi_p\}$ representation of (11),

$$\mathbf{F}' \mathbf{C}_i = \lambda_i \mathbf{S} \mathbf{C}_i. \quad (12)$$

Defining $\mathbf{R} = \mathbf{C} \mathbf{C}^\dagger$ and noting that $\mathbf{R}^\dagger \mathbf{S} \mathbf{R} = \mathbf{R}$ and $\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1}$ we can express

$$\mathbf{F}' = \mathbf{F} + \mathbf{V}_1 - \mathbf{S} \mathbf{R} \mathbf{V}_1 - \mathbf{V}_1 \mathbf{R} \mathbf{S} + \mathbf{S} \mathbf{R} \mathbf{V}_1 \mathbf{R} \mathbf{S} + \mathbf{S} \mathbf{R} \mathbf{V}_2 \mathbf{R} \mathbf{S}, \quad (13)$$

where $\mathbf{V}_1 = \mathbf{X}^\dagger \Omega_{1\alpha} \mathbf{X}$ and $\mathbf{V}_2 = \mathbf{X}^\dagger \Omega_{2\mu} \mathbf{X}$.

Under CNDO approximations the overlap is neglected in normalization. Thus, $\mathbf{S} = \mathbf{1}$ and $\mathbf{R} \equiv \mathbf{P}$ which is the matrix representation of projector P_A in the orthonormalized basis. Equation (13) is simplified to

$$\mathbf{F}' = \mathbf{F} + (\mathbf{1} - \mathbf{P}) \mathbf{V}_1 (\mathbf{1} - \mathbf{P}) + \mathbf{P} \mathbf{V}_2 \mathbf{P}. \quad (14)$$

Simplification from CNDO entails

$$(\mathbf{V}_1)_{pq} = a_1 \sum_r c_{r\alpha}^2 g_{pr} \delta_{pq} + b_1 c_{p\alpha} c_{q\alpha} g_{pq},$$

$$(\mathbf{V}_2)_{pq} = a_2 \sum_r c_{r\mu}^2 g_{pr} \delta_{pq} + b_2 c_{p\mu} c_{q\mu} g_{pq}.$$

It should be noted that the two operators $\Omega_{1\alpha}$ and $\Omega_{2\mu}$ have a mutual interdependence and that (12) and (14) must be solved iteratively. At convergence the excited state energy is calculated as

$$E = E_0 + \lambda_\mu - \lambda_\alpha - a_1 J_{\alpha\mu} + b_1 K_{\alpha\mu}. \quad (15)$$

With the objective of removing the nonorthogonality problem in the HPPM theory it is convenient to formulate the average Fock operator

$$\begin{aligned} F' = F + P_B^\dagger (\Omega_{1\alpha} + \Omega_{1\beta}) P_B + P_A^\dagger (\Omega_{2\mu} + \Omega_{2\nu}) P_A \\ + \sum_{\alpha}^{n_A} f_{\alpha} [P_B^\dagger (J_{\alpha} - K_{\alpha} \mp K_{\alpha}) P_B], \end{aligned} \quad (16)$$

where f_{α} and f_{μ} are orbital weight parameters.

In quite a similar manner the Fock operator corresponding to the doubly excited configuration $\Psi_{(\alpha\beta \rightarrow \mu\nu)}$ can be formulated as

$$F' = F + P_B^\dagger (\Omega_{1\alpha} + \Omega_{1\beta}) P_B + P_A^\dagger (\Omega_{2\mu} + \Omega_{2\nu}) P_A. \quad (17)$$

Our present work concerns singly excited configurations only and (11) and (14) are employed in computing excited states of the thiocarbonyls.

3. Results and discussion

We present the results of our calculation and the related discussion about the chosen thiocarbonyl molecules under three headings. Firstly, we discuss the salient features of techniques employed in computation, difficulties encountered and their origin are given some rationale in terms of known information. Secondly, we present our results of molecular excited state conformation together with a comparison with the HPM results and the available experimental values. Since the

molecules H_2CS , HFCS and F_2CS have already been studied in the context of HPM theory, it is pertinent to consider the same ones in order to judge the merit of the present HPPM theory. Thirdly, electronic transition energies and relative ordering of the low lying $n\pi^*$ and $\pi\pi^*$ states are investigated.

3.1 Computational approach

As it is apparent that the quantities a_{kl} and b_{rs} in (1) represent coupling between orbitals belonging to different subspaces, it is expected that eigenvalues from operator F' in (11) includes a double correction in considering the interaction between orbitals ψ_α and ψ_μ . Hence the need for the correction made in (15). While not giving the eigenvalues from (14) the same significance as orbital energies in the Koopman's sense, it is found that the modified upper orbital eigenvalues λ_μ are lower in magnitude than λ_α , the corresponding eigenvalues of the lower orbitals in a particular excited state. This situation requires a constant level shifting up (Saunders and Hillier 1973) of the upper orbitals during the iteration and after each diagonalization the shift amount is subtracted from all the transformed upper orbital eigenvalues. This resulted in a smooth convergence in most cases due to prevention of the undesirable inter-subspace orbital swapping.

In cases of substantial orbital reorganization in either or both subspaces there occurs intra-subspace orbital swapping during the iteration. As for example, the n -orbital may be the HOMO and the immediately underlying orbital may be a π , whereas LUMO is a π^* in the ground state wavefunction of some carbonyl compound. To start with, the $n\pi^*$ excitation is from HOMO to LUMO. After some iterations the n -orbital may go down below the π orbital which then becomes the 'HOMO'. In order to keep the correct configuration for the excited state throughout the entire calculation, arrangement must be done to identify the appropriate ψ_α and ψ_μ before each iteration. Since the symmetry of each MO is uniquely defined under the molecular point group, an account of the symmetry of all the MO belonging to both subspaces are stored in the memory in the form of character string arrays. At the beginning of each iteration particular orbital pairs are located by their symmetry by comparison of such arrays. In table 1 we present a SCF convergence profile for the $^3A''(n\pi^*)$ state of F_2CS molecule at a near equilibrium (40° bent out of plane) geometry. In the beginning, the n -orbital was 12th in the usual ordering, but at convergence it became the 11th, while the

Table 1. Convergence profile for the $^3A''(n\pi^*)$ state of the F_2CS molecule in a 40° bent out-of-plane geometry.

Iteration number	Electronic energy (a.u.)	$(\lambda_\mu - \lambda_\alpha)$	$J_{n\pi^*}$	$K_{n\pi^*}$
1	-73.0031988	-0.2404079	0.3727068	0.0003076
2	-73.0155678	-0.2530753	0.3730054	0.0002899
3	-73.0157237	-0.2533755	0.3731497	0.0002893
4	-73.0158648	-0.2535198	0.3731528	0.0002891
5	-73.0158665	-0.2535230	0.3731543	0.0002891
6	-73.0158679	-0.2535245	0.3731543	0.0002891
7	-73.0158680	-0.2535245	0.3731543	0.0002891

π -orbital became 12th in position. The lowest π^* orbital, however, retained its position unaltered as the 13th.

In all our calculations the singlet multiplicity state has always been found to be energetically higher than the corresponding triplet counterpart arising from a similar orbital configuration, except for the $n\pi^*$ states in the planar geometry. This unfortunate situation arises due to the neglect of all one centre exchange integrals in the CNDO approximation. The singlet-triplet degeneracy in the planar geometry occurs due to vanishing of the $K_{n\pi}$ integral under such approximation.

One remarkable feature was explored when our HPPM SCF method was employed for the calculation of $^1\pi\pi^*$ species which cannot be distinguished on the basis of orbital symmetry characteristics from other lower energy species, including the ground state. Whereas the $^3\pi\pi^*$ species converged smoothly at all conformations of bending, the corresponding $^1\pi\pi^*$ state did not converge even at the slightest departure from planarity. The planar $^1\pi\pi^*$ species converged, however with difficulty after a very extensive reorganization of the orbitals, accompanied in all cases with drifting of both the π and π^* orbitals to a greater blue shift region (see table 5 below). The resulting excitation energies show a higher magnitude and cannot be reasonably accepted unless corrected for the loss of orthogonality with the ground state. It may be noted that excited states arising from $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ excitations with singlet spin coupling are generally described as semidiffuse in character (Peyerimhoff and Buenker 1975) rather than as valence species type. Such a situation requires incorporation of long range diffuse functions in the basis set (Huzinaga 1962) for an adequate representation of the excited state. It is felt therefore, that in calculating such semidiffuse states reliably, *ab initio* calculations with double-zeta basis, augmented with appropriate diffuse functions should be employed keeping in mind, however, the maintenance of the orthogonality of such states.

3.2 Structural results

In table 2 we present the equilibrium out-of-plane bending angles in $^{1,3}n\pi^*$, $^3\pi\pi^*$ states of H_2CS , HFCS and F_2CS . Results from unrestricted open-shell (^3UHF)

Table 2. Out-of-plane bending equilibrium angles in $^{1,3}n\pi^*$ and $^3\pi\pi^*$ states of tetra-atomic thiocarbonyls. Quantities within ()^a represent HPM calculated results and those within [] represent experimental/*ab initio* values.

Molecule	Bending angle (degrees)			
	$^3n\pi^*$	$^1n\pi^*$	$^3\pi\pi^*$	^3UHF
H_2CS	30(30) [24.2] ^b	20(20)	12(10) [13] ^d	0
HFCS	37(35) [35.2] ^b	33(35)	33(30)	25
F_2CS	38(40) [42] ^b [30.5–34.1] ^c	39(40)	40(40)	32

^aBanerjee and Bhattacharyya (1980, 1983); ^bKapur *et al* (1979);

^cMoule and Mehra (1970); ^dBruna *et al* (1974).

Table 3. *p*-electron and *s*-electron densities on the C-atom in planar and equilibrium nonplanar geometries in the $^1,^3n\pi^*$ and $^1,^3\pi\pi^*$ states of some thiocarbonyls.

Molecule	Geometry	C-atom orbital	One-electron density in			
			$^3n\pi^*$	$^1n\pi^*$	$^3\pi\pi^*$	$^1\pi\pi^*$
H ₂ CS	Planar	<i>p</i>	3.3610	3.3610	2.9966	2.9966
		<i>s</i>	1.1506	1.1506	1.1506	1.1506
	Equil ^a	<i>p</i>	3.3025	3.3234	2.9841	—
		<i>s</i>	1.1844	1.1722	1.1556	—
HFCS	Planar	<i>p</i>	3.1653	3.1653	2.9165	2.9428
		<i>s</i>	1.1478	1.1478	1.1486	1.1486
	Equil	<i>p</i>	2.9711	3.0282	2.8317	—
		<i>s</i>	1.2351	1.2226	1.2074	—
F ₂ CS	Planar	<i>p</i>	2.9810	2.9810	2.8239	2.8404
		<i>s</i>	1.1562	1.1562	1.1562	1.1562
	Equil	<i>p</i>	2.6510	2.6538	2.5582	—
		<i>s</i>	1.3172	1.3152	1.2866	—

^aEquil = Nonplanar equilibrium (adiabatic) geometry.

calculations are included for comparison. In all calculations *d*-orbitals were excluded from the basis set of the S-atom, as it was found in earlier HPM calculations (Banerjee and Bhattacharyya 1980) that inclusion of such basis functions destroy the geometrical features of excited states. It may be observed from table 2 that the equilibrium angles of non-planarity in our present calculation are almost comparable to those found by HPM calculations. In H₂CS the extent of nonplanarity is greater in the $^3n\pi^*$ state than in the $^1n\pi^*$ state. With gradual fluorine substitution the difference in their extents of nonplanarity decreased almost uniformly. The simple HPM results were rather insensitive in that they predicted equal amounts of bending in both singlet and triplet $n\pi^*$ states of HFCS and F₂CS. It is encouraging to note that the predicted bending (38°) in $^3A''$ of F₂CS has better agreement with experimental results (30.5°–34.1°) than the *ab initio* open-shell (STO-3G) calculated magnitude (42°). A decreasing trend of the electron density on the C-atom in the different equilibrium excited state conformations of the three molecules is observed (table 3) with increasing fluorine substitution. This is in keeping with the gradual electron-withdrawing effect by the electro-negative fluorine atoms. Close observation reveals that inspite of this gradual decrease in total electron density on the C-atom, there is an opposite increasing trend in the *s*-electron density in these molecules which, obviously, is compensated by a greater diminishing trend in *p*-electron density. The trend of increasing nonplanarity in a particular state in all the three molecules can be expected from the Walsh postulate (Walsh 1953) that 'whether or not an orbital becomes more tightly bound with change of angle is determined primarily by whether or not it changes from being built from a *p*-orbital (on an atom) to being built from an *s*-orbital (on that atom)'.

The barriers to inversion estimated by such semiempirical methods are always expected to predict high values due to the deficiency inherent in the CNDO theory. Still the present method yields barrier heights which are better than those predicted by the simple HPM theory (table 4). Successive fluorine substitution leading to gradual withdrawal of electron density from the C-atom seems to enhance the barrier height in all cases.

3.3 Spectral results

Adiabatic (with respect to nonplanar bending) and vertical transition energies for $A \leftarrow \tilde{X}$ transitions in the three molecules considered are presented together with the UHF-calculated results in table 5. In H_2CS the presently calculated magnitudes

Table 4. Barrier to planar inversion (in cm^{-1}) in excited states of thiocarbonyls; quantities within ()^a represent HPM results, those within [] are experimental/*ab initio* results.

Molecule	Planar inversion barrier in			
	$^1n\pi^*$	$^3n\pi^*$	$^3\pi\pi^*$	^3UHF
H_2CS	86 (285)	385 (394) [108] ^b	11 (≈ 0)	0
HFCS	1256 (4321)	2130 (5418) [843] ^b	972 (1082)	304
F_2CS	5934 (6032)	6230 (6186) [> 3100] ^b	4415 (4345) [> 3000] ^c	1786

^aBanerjee and Bhattacharyya (1980, 1983); ^bKapur *et al* (1979);

^cLessard and Moule (1973).

Table 5. $^1,^3n\pi^*$ and $^1,^3\pi\pi^*$ transition energies (eV) in some simple thiocarbonyls. Quantities within ()^a represent HPM calculated results, those within [] are experimental or *ab initio* values.

Molecule	Transition energy in eV							
	$^3n\pi^*$		$^1n\pi^*$		$^3\pi\pi^*$		$^1\pi\pi^*$	^3UHF
	Adiabatic	Vertical	Adiabatic	Vertical	Adiabatic	Vertical	Vertical	Vertical
H_2CS	3.11 (3.10) [2.3-2.5] ^b	3.15 (3.15)	3.14 (3.12)	3.15 (3.15)	3.73 (3.72) [3.28] ^c	3.73 (3.72)	20.48	1.86
HFCS	3.77 (4.34)	4.04 (5.01)	3.88 (4.48)	4.04 (5.01)	4.08 (4.03)	4.20 (4.17)	18.38	2.57
F_2CS	4.29 (4.29) [3.00] ^d	5.06 (5.05)	4.32 (4.30)	5.06 (5.05)	4.22 (4.17) [6.08] ^e	4.77 (4.80)	16.38	3.25

^aBanerjee and Bhattacharyya (1980, 1983); ^bPeyerimhoff and Buenker (1975); ^cBruna *et al* (1974); ^dMoule and Mehra (1970); ^eLessard and Moule (1973).

Table 6. Energy differences and decrease in electron population on C-atom in passing from $^3n\pi^*$ state to $^3\pi\pi^*$ state in the thiocarbonyls

Molecule	$E_{\pi\pi^*} - E_{n\pi^*}$ (eV)	Decrease in electron population on C (vertical)
H ₂ CS	0.620	0.3644
HFCS	0.305	0.2480
F ₂ CS	-0.064	0.1571

are in very close agreement with the simple HPM results. This reflects that hole orbitals reorganization should be small. The reasons for exceptionally high values for the $^1\pi\pi^*$ transition energies seem to have been explained in §3.1 and it appears (Peyerimhoff and Buenker 1975) that the corresponding CI calculated values, viz. 11.41 eV in H₂CO and 7.92 eV in H₂CS are large enough to find such states to be located high up in the spectrum. From a comparison of the HPM and HPPM results in all the three molecules it is observed that the effect of hole orbitals reorganization, which results in a difference in transition energies in the two methods, is most prominent in the case of $n\pi^*$ transitions in HFCS. It may be noted that unrestricted open-shell transition energies in H₂CS and F₂CS are in better agreement with the corresponding experimental values observed for their lowest triplets. While such betterment can be ascribed to a greater variational flexibility of the UHF method, compared to our HPPM, the former suffers from non-specificity of the particular excited state.

One can observe from tables 5 and 6 that the energy difference between $^3\pi\pi^*$ and $^3n\pi^*$ states decrease along the sequence H₂CS → HFCS → F₂CS, so much so that in F₂CS there is just a reversal in the order of $\pi\pi^*$ and $n\pi^*$ states. As the n -orbital is centred mainly upon the S-atom and the π^* orbital, although delocalized, has a greater amplitude on the C-atom, the $n \rightarrow \pi^*$ excitation leads to a flow of electron density from sulphur to carbon. On the other hand, the $\pi \rightarrow \pi^*$ excitation is well delocalized over the C=S region. In passing from a $n\pi^*$ state to a $\pi\pi^*$ state one finds from table 5 that there is a decrease in electron density on the carbon atom. Gradual attachment of the electronegative fluorine atoms with carbon is expected to withdraw the excess build-up of electron density on C in the $n\pi^*$ state, thereby levelling off the difference between $^3n\pi^*$ and $^3\pi\pi^*$ states. The predicted reversal in the order of low lying triplets in F₂CS is not quite unusual as it is evident that similar inversions are known to occur with some aromatic carbonyls. The failure to undergo photoreduction (Turro 1965) by 2-acetonaphthone and 1-naphthaldehyde with alcohols under the usual conditions is attributed to the existence of the $^3\pi\pi^*$ state as the lowest lying T_1 state. The reason has been the delocalization of electron density from the carbonyl region. It should, therefore, be worthwhile in the context of our present study to compare the relative ease of photoreduction of these thiocarbonyls.

4. Conclusion

Although the open-shell method of Morokuma is nothing new at the present time, its formulation in the framework of semiempirical model like the CNDO is

definitely substantial in the context of application to moderately large-size molecular systems in retrieving at least qualitative information about the relative ordering of the various excited states and about the excited state geometry, barrier height etc. A serious limitation to improvement in this method is imposed by the extremely small size of the valence AO basis set employed in CNDO calculation. In future calculations employing extended basis sets, the results are expected to improve further. The most noteworthy point is that the one-electron orbitals thus obtained in calculating a particular excited state are more suitable in providing the expansion for that state, rather than the usual Hartree Fock MO which sometimes fail to produce any improvement in such excited state calculations.

Acknowledgement

The authors wish to express their sincere thanks to Dr S P Bhattacharyya for helpful discussions. One of the authors (AKC) is grateful to the UGC for fellowship. Computation facilities were extended by the personnel of the Computer Centre.

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On the use of dipole moment as a collective coordinate in constrained variational calculations

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Abstract. The dipole moment function of a diatomic molecule may be viewed as a continuous collective coordinate which encodes a lot of information about sharing of electrons between the atoms concerned. By its very nature it takes cognizance of certain many-body effects and should shape the constrained wavefunction or the one electron density in much the same way as would explicit inclusion of the same many-body effects. A case study of the problem with lithium hydride as the model system has been presented and the long range behaviour of the constrained density analysed. The spectrum of the constrained Fock operator is compared with that of the unconstrained one.

Keywords. Constrained variation; direct determination of density; penalty function method; dipole moment as a collective coordinate.

1. Introduction

The variational method is a very useful technique in atomic and molecular calculations of electronic structure and properties. Among the properties of a system, energy has a special status in that it is always estimated one order of magnitude better than the other non-commuting observables. Energy, therefore can *not* reflect the *error* in an approximate variational wavefunction as much as the other properties (observables $\{\hat{A}_k\}$ not commuting with $\hat{H}$). The constrained variational method (CVM) was developed in this context. Essentially what one does in CVM is try to minimize energy subject to the minimization of errors in the expectation values of number of chosen observables (Mukherjee and Karplus 1963; Rasiel and Whitman 1965; Chong and Rasiel 1966) without increasing the variational flexibility of the trial wavefunction any further from that already present in the unconstrained trial function. This, however, entails some sacrifice in energy (Byers Brown 1966). The particular choice of constraining observables is conditioned by the purpose at hand. Thus, if one wishes to use the constrained wavefunction as an alternative starting point in a configuration interaction or perturbative calculation with a view to accelerating the convergence, a property which delicately depends on the behaviour of the wavefunction close to the nucleus is the obvious choice. Alternatively one may use the nuclear cusp condition as a suitable theoretical constraint on the wavefunction. For some other purposes, experimental values of electric dipole moment, quadrupole moment etc could be useful. Of the different observables the dipole moment (μ_{AB}) of a diatomic species AB offers some interesting possibilities as a constraining parameter. These possibilities hinge on the fact that μ_{AB} can be treated as a continuous collective

coordinate (right from the united atom to the separated atom limit) which has encoded in it very significant information concerning the sharing of electron density between the atom-pair (A, B) and deformation of the atomic density on molecular formation. By its very nature $\mu_{AB}(R)$ takes into account certain many-body effects and when used as a constraint would possibly shape the constrained wavefunction or the one-electron density in much the same way as explicit inclusion of these effects would have done. Hence, if the dipole moment function $\mu_{AB}(R)$ of AB in a particular electronic state (say, the ground state) be known, it can be used as a constraint to obtain what may be called a dipole constrained potential energy curve. A question of immediate interest concerns the type and the extent of reorganization of electron density induced by the constraint over the whole range of R and particularly in the large R regions. More interestingly, one may think of treating the internuclear separation R_{AB} and $\theta_{AB}(\theta_{AB} = \mu_{AB}/R_{AB})$ as two independent collective coordinates and try to obtain an energy map in the (R, θ) plane. Among other things, these maps can throw light on the existence of metastable states, nature of bonding or existence of alternative channels of dissociation, if any (viz $A + B$, $A^+ + B^-$, $A^{+2} + B^{-2}$ etc). The basic purpose of the present work is to investigate some of the aforementioned possibilities.

2. The problem

The system of our choice is the lithium hydride molecule. The ground state dipole moment curve of lithium hydride is known quite accurately (Patridge and Langhorne 1981). The special feature of the μ - R profile of lithium hydride lies in an inversion displayed by it. The absolute value of μ_{LiH} first increases, attains a maximum and decays to zero as $R \rightarrow \infty$. This inversion followed by a decay to zero value cannot be recovered in a single configuration SCF calculation, *ab initio* or semiempirical. Obviously, this is related to the basic inadequacy of the single configuration description of the wavefunction. Could a μ -constrained calculation at the Hartree-Fock level generate the correct μ - R profile and simultaneously improve the quality of the wavefunction or the one-electron density in the large- R regions? We investigate these questions in what follows. The calculations are made at an all valence semiempirical (CNDO/2) level of approximation and the constrained variational calculations are carried out by using a method for the direct determination of constrained pure state electron density in a discrete orthonormal basis developed by us (Das and Bhattacharyya 1986; Das *et al* 1985).

3. The method

Let us consider a $2m$ -electron closed-shell molecule described in terms of one-electron density matrix P in an n -dimensional discrete orthonormal basis $\{\chi_i\}_{i=1, n}$. We demand that in addition to the N -representability constraints on $(P^2 = P, P^+ = P$ and $Tr p = m)$ there is an additional constraint that P must minimize energy subject to the condition that

$$2 \text{Tr}\{PD\} = d_0, \quad (1)$$

where D represents the electric dipole matrix in the χ -basis and d_0 is the actual (known) dipole moment of the system. The variational determination of P subject to the constraint in (1) can be done in a number of ways. The general strategy for handling a problem of this kind, recently developed by us (Das and Bhattacharyya 1986) requires a start, in the present case, with the functional $\varepsilon(E, E_L, \sigma, \lambda; P)$, where

$$\varepsilon(E, E_L, \sigma, \lambda; P) = (E - E_L)^2 + \sigma \text{Tr}(P^2 - P)^2 + \lambda [\text{Tr}\{PD\} - d_0]. \quad (2)$$

In (2), σ is a penalty weight factor of appropriate dimension and magnitude, λ is the Lagrangian multiplier connected with the constraint in (1) and E_L is an estimated lower bound to the constrained energy. Minimization of ε leads to the following iterative scheme for the determination of P :

$$P_{i+1} = 3P_i^2 - 2P_i^3 - \alpha(E_i - E_L^i)F_i - \gamma_i D, \quad (3)$$

where $\alpha = 2/\sigma$ and $\gamma = \lambda/\sigma$ and

$$F_i = h + G(P_i); \quad G(P_i) = 2J(P_i) - K(P_i).$$

The Lagrangian parameter γ_{i+1} is determined by the condition

$$2\text{Tr}\{P_{i+1}D\} = d_0, \quad (4)$$

which leads to the result that

$$\gamma_{i+1} = 2[\text{Tr}\{Q_i D\} - d_0] / \text{Tr}\{D^2\}, \quad (5)$$

where,

$$Q_i = 3P_i^2 - 2P_i^3 - \alpha(E_i - E_L^i)F_i.$$

The $(i+1)$ th approximation to the lower bound E_L^{i+1} can be obtained by adopting the method of Fiocco and McCormik (1968), which in the present case takes the following form

$$E_L^{i+1} = E_L^i - \beta \text{Tr}\{A_i^\dagger A_i\}^{1/2}, \quad (0 < \beta \leq 1), \quad (6)$$

where,

$$A_i = \alpha(E_i - E_L^i)F_i + (2P_i^3 - 3P_i^2 + P_i) + \gamma D.$$

The iterations represented by (3) were terminated when $\text{Tr}\{A_i^\dagger A_i\} < 10^{-6}$ in each calculation.

4. Results and discussion

4.1 Large- R behaviour of the constrained density

The constrained calculations correctly reproduce all the details of the actual μ - R profile (table 1) including the inversion at the correct value of R . We have already reported that the force constant improves remarkably (Das *et al* 1987) due to the constraint. In the present study, our main interest lies in the large- R behaviour of the constrained density. Table 2 summarises variations in the net charge density on lithium and hydrogen atoms over a large range of internuclear separation both in

Table 1. Comparison of the actual ground state dipole moment function of LiH with those predicted by the unconstrained and the μ -constrained Hartree-Fock (semiempirical) methods.

R (a.u.)	μ Hartree-Fock (Debye)	μ Constrained HF (Debye)	μ Actual (Debye)
1.75	6.86	4.837	4.840
2.00	6.85	4.946	4.950
2.25	6.75	5.11	5.11
2.50	6.59	5.31	5.31
2.75	6.39	5.55	5.56
3.00	6.15	5.81	5.81
3.25	5.88	6.08	6.08
3.50	5.60	6.35	6.35
4.00	4.97	6.88	6.88
5.00	3.54	7.56	7.56
5.56	2.77	7.48	7.48
6.00	1.96	6.93	6.93
8.00	1.48	1.97	1.97
10.00	4.97	0.05	0.05

Table 2. Comparison of constrained and unconstrained charge densities on Li and H atoms at various internuclear separations of Li-H.

R_{Li-H} (a.u.)	Unconstrained HF results: net charge density on		Constrained Hartree-Fock results: net charge density on	
	Li atom	H atom	Li atom	H atom
2.00	0.2632	-0.2632	0.3776	-0.3776
2.75	0.2678	-0.2678	0.3139	-0.3139
3.00	0.2715	-0.2715	0.2896	-0.2896
3.75	0.2873	-0.2873	0.2235	-0.2235
4.50	0.3078	-0.3078	0.1742	-0.1742
5.00	0.3226	-0.3226	0.1552	-0.1552
5.50	0.3370	-0.3370	0.1506	-0.1506
7.00	0.3694	-0.3694	0.2240	-0.2240
8.00	0.3844	-0.3344	0.2750	-0.2750
10.00	0.3858	-0.3858	0.2530	-0.2530

the unconstrained and the μ -constrained descriptions of the molecule. The constrained calculations are seen to predict a higher degree of polarity of the Li-H molecule at shorter values of R ($R < R_0$) compared to the polarity in the unconstrained description. But as R increases, the constraint effectively forces more and more electron density to flow from $H \rightarrow Li$ (compared to the unconstrained results) signifying that the constrained potential energy curve is a better one and may perhaps lead to the correct dissociation limit. A perusal of table 2 clearly shows that although the polarity of the Li-H molecule is far less in the constrained description at all the larger values of R , the polarity does not decrease monotonically as $R \rightarrow \infty$. It decreases monotonically upto a certain value of R ($= R_c$, say). Beyond $R = R_c$, $Li \rightarrow H$ transfer of electron density (compared to

that observed for $R < R_c$) seems to increase progressively (table 2) even in the constrained calculations, although the degree of $\text{Li} \rightarrow \text{H}$ electron transfer remains far less pronounced compared to that found in the unconstrained Hartree-Fock description. The constrained dipole moment, however, vanishes beyond $R > 10.0$ a.u. as demanded. This failure of the constrained PE curve to lead to the correct dissociation limit ($\text{Li} + \text{H}$) even though the *limiting zero dipole moment value is correctly reached* may appear to be intriguing at first sight. But it arises quite naturally due to the following reason. Within the framework of our basic approximations (CNDO/2), the ground state dipole moment of LiH can be resolved into two separate contributions: (a) that due to charge separation in the molecule (μ_{charge}); (b) that due to the mixing or hybridization of $2s$ and $2p_z$ basis function on the Li atom (this destroys the spherical symmetry of the Li-electron density) (μ_{hyb}). The zero dipole moment in the large R -limit ($R > 10$ a.u.) is reached in the constrained calculation not by forcing μ_{charge} and μ_{hyb} to vanish separately, but by forcing them to cancel each other as the internuclear separation increases beyond a particular value ($R = 10$ a.u.). The μ -constrained dissociation limit of Li-H is thus different from both the unconstrained Hartree-Fock and the actual dissociation limits. In table 3 we have compared the constrained and unconstrained densities at $R = 10.0$ a.u. It is clear that the (i) net charge separation in the constrained case is less than that in the unconstrained one, (ii) $2s-2p$ mixing of Li orbitals in the constrained case is larger than its unconstrained counterpart; (iii) an enhanced electron population in the lithium $2p_\sigma$ orbital is found in the constrained calculation compared to the unconstrained one. Apparently therefore, the dissociation limit in the constrained one-configuration calculation has higher weightage of products like $\text{Li} (2p)$ compared to what one finds in the HF dissociation limit and of course, a lesser degree of weightage of the ionic products like Li^+ and H^- . The use of the additional constraint, $\mu_{\text{hyb}} = 0$, for all values of R may possibly bring about the correct homopolar dissociation. This is being explored at present. Thus although the collective coordinate for a diatomic molecule does possess very significant information about electron sharing between the atoms A and B at various internuclear separations, it can *not* as such recover the correct dissociation limit when used as the *only* constraining observable if one works in the framework of single determinant representable densities. However, it does modify the dissociation limit. It may be possible therefore to use θ as a collective coordinate in the construction of an energy map in the (R, θ) plane and it

Table 3. Comparison of the unconstrained (i.e. Hartree-Fock) and the μ -constrained electron densities for Li-H in the ground state at a large internuclear separation ($R = 10.0$ a.u.).

Atom/basis function		Electron density (χ_i)		Degree of $2s-2p_z$ mixing on Li-atom	
(A)	(χ_i)	HF results	CHF results	HF results	CHF results
Li/	$2s$	0.5194	0.6126	0.2220	0.2870
	$2p_x, 2p_y (\pi)$	0.0	0.0		
	$2p_z (\sigma)$	0.0056	0.1244		

may reveal new information on the existence of metastable states of the diatomic system used.

4.2 Constrained versus unconstrained orbitals

The set of orbitals $\{\phi_i^0\}$ that diagonalise the unconstrained minimum energy idempotent one-electron density matrix (P_0) are the Hartree-Fock orbitals (HFO). The orbital set that diagonalises the constrained idempotent one-electron density matrix (P_c) represent a set of natural orbitals $\{\phi_i^c\}$ which may be called the constrained Hartree-Fock orbitals (CHFO). $\{\phi_i^0\}$ diagonalises the unconstrained Fock operator F^0 ($F^0 \phi_i^0 = \phi_i^0 \epsilon_i^0$; $F^0 = h + \nu_{\text{HF}}(\phi_i^0)$). Similarly, $\{\phi_i^c\}$ satisfy the following eigenvalue equation

$$F^c \phi_i^c = \phi_i^c \epsilon_i^c,$$

where

$$F^c = h + \nu_{\text{HF}}(\phi_i^c).$$

One may use the set $\{\phi_i^c, \epsilon_i^c\}$ as an alternative starting point in perturbative or ϵ calculations of energy or other properties, may be, with better convergence properties. To have some idea about the disposition of the spectrum of the constrained and the unconstrained Fock operators we have compared in table 4 the HFO and CHFO for lithium hydride at $R = 7.0$ a.u. A perusal of table 4 clearly reveals that the 3σ MO is more localised on the hydrogen atom in the unconstrained calculation than predicted by the dipole constrained approximation. The two unoccupied σ orbitals (4σ , 5σ) are also affected by the constraint, albeit indirectly. The corresponding orbital energies indicate that the constraint stabilises 3σ and 4σ orbitals (relative to the unconstrained ones) but destabilises all other

Table 4. A comparison of the eigenspectrum of the unconstrained and the constrained Fock operator for lithium hydride molecule at $R = 7.00$ a.u. The calculations were done at a semiempirical level (CNDO/2) using dipole moment as the constraint.

MO/AO basis		Unconstrained	Unconstrained	Constrained AO	Constrained
		AO amplitudes	orbital energy	amplitudes	orbital energy
		(C_{pi}) in ϕ_i^0	ϵ_i^0	(C_{pi}) in ϕ_i^c	ϵ_i^c
3 σ Li	2s	0.4522		0.4949	-0.2878
	2p _z	0.3320	-0.2603	0.3783	
	2p _x , 2p _y	0.0, 0.0		0.0, 0.0	
H	1s	0.8275		0.7823	
4 σ Li	2s	0.8917			
	2p _z	-0.1488	-0.0328	0.8101	-0.0332
	2p _x , 2p _y	0.0, 0.0		0.1248	
π			0.0371, 0.0371	0.0, 0.0	
	H 1s	-0.4275		-0.5728	
Li	2p _x , 2p _y	1.0, 1.0	0.0371, 0.0371	1.0, 1.0	0.0506, 0.0506
5 σ Li	2s	-0.1920		-0.3143	
	2p _z	0.9312		0.9172	
	2p _x , 2p _y	0.0, 0.6		0.0, 0.0	
H	1s	-0.3641	0.0466	-0.2447	0.0513

unoccupied orbitals. The constraint therefore shifts the entire spectrum of F^c relative to F^0 . Clearly, the rate of convergence of a perturbative series or CI expansion will be different when $\{\phi_i^c, \epsilon_i^c\}$ are used as basis functions. However, a priori theoretical analysis of the effects of a particular constraint on the rate of convergence of the corresponding perturbative or CI series is a formidable task and is being studied at present. We hope to return to this aspect in the near future.

Acknowledgement

The authors are grateful to the DST, Government of India, for a research grant.

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A valency method for the prediction of geometry of molecular excited states

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Abstract. A simple method, based on the concept of molecular valency and making use of the virtual orbitals of the ground state, is proposed to predict the geometry of molecules in various excited and ionised states. The method is found to be accurate for bond angle predictions.

Keywords. Molecular valency; excited state geometry; bond angle predictions.

1. Introduction

Theoretical calculations of the geometry of excited states of molecules usually proceed by determining the minimum point on a molecular potential energy surface by a point-by-point mapping through successive calculations of the total energy. Since wavefunctions at the configuration interaction (CI) level are required to achieve a fair degree of accuracy, such calculations become very costly in terms of computer time. Moreover a mere energy calculation, however sophisticated, does not by itself lead to an understanding of the chemical factors determining molecular shape. Further analysis of the wavefunction is required for this purpose, which is difficult at the CI level. In this paper, we propose a simple method for the determination of excited state geometries of molecules, using the ground state wavefunctions alone, based on the concept of valency.

2. The method

Valency of an atom A in a molecule has been defined previously (Armstrong *et al* 1973; Gopinathan and Jug 1983; Gopinathan 1986) as:

$$V_A = \sum_{B \neq A} \sum_a^A \sum_b^B P_{ab}^2 \quad (1)$$

where P_{ab} is the density matrix element between the orbitals a on atom A and b on atom B in an orthogonal basis. From (1), expressions for molecular orbital valency v_i and molecular valency V_M have been obtained (Gopinathan *et al* 1986):

$$v_i = \frac{1}{2} \sum_A \sum_a^A \sum_{B \neq A} \sum_b^B \sum_j n_i n_j C_{ia} C_{ib} C_{ja} C_{jb}, \quad (2)$$

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$$V_M = \sum_i V_i = \frac{1}{2} \sum_A V_A, \quad (3)$$

where n_i is the occupancy of the i th molecular orbital (*mo*). (1) and (2) apply to closed shell molecules. For open shell systems, since in general $C_{ia}^\alpha \neq C_{ia}^\beta$, one should use the following generalisations of (1) and (2).

$$\begin{aligned} V_A &= \sum_{B \neq A} \sum_a^A \sum_b^B (P_{ab}^\alpha + P_{ab}^\beta)^2, \\ V_i &= \frac{1}{2} \sum_A \sum_a^A \sum_{B \neq A} \sum_b^B \sum_j [n_i^\alpha n_j^\alpha C_{ia}^\alpha C_{ib}^\alpha C_{ja}^\alpha C_{jb}^\alpha \\ &\quad + n_i^\beta n_j^\beta C_{ia}^\beta C_{ib}^\beta C_{ja}^\beta C_{jb}^\beta + n_i^\alpha n_j^\beta C_{ia}^\alpha C_{ib}^\beta C_{ja}^\beta C_{jb}^\alpha \\ &\quad + n_i^\beta n_j^\alpha C_{ia}^\beta C_{ib}^\alpha C_{ja}^\alpha C_{jb}^\beta], \end{aligned} \quad (4)$$

where P_{ab}^σ ($\sigma = \alpha$ or β) is the spin polarised density matrix element. These valency quantities have been well studied and correlated with determination of structure (Gopinathan *et al* 1986), strain (Siddarth and Gopinathan 1986), and reaction pathways (Jug and Gopinathan 1985). In particular, we have shown earlier (Gopinathan *et al* 1986) that for the ground state, molecular valency reaches a maximum at the equilibrium bond angle and that molecular orbital valency serves as a quantitative ordinate for the well-known Walsh diagrams (Walsh 1953). Thus the equilibrium bond angle of molecules in their ground states can be determined quite accurately by means of either the molecular valency V_M or the molecular orbital valency V_i .

We now investigate whether the excited state bond angles also can be similarly predicted from valency. The procedure we adopt is as follows:

- A ground state calculation of the molecule at various bond angles is performed.
- Excited or ionised electronic configurations of the molecule are obtained simply by making use of the occupied and virtual orbitals from (a) as required.
- Molecular orbital valency and molecular valency at a particular bond angle are now calculated by using (2), (4) and (3), with the MO occupancies and coefficients determined as in (b).
- The equilibrium bond angle is then given by that angle for which molecular valency V_M is a maximum.

3. Results

We have presently calculated the bond angles for several excited as well as ionised states of some triatomic molecules as described above. Calculations were done using *ab initio* STO-3G Löwdin-orthogonalised wavefunctions. Table 1 presents the bond angles obtained by the present valency method as well as the results of previous *ab initio* calculations and available experimental data for the sake of comparison. We have also plotted $\Delta V(\theta)$, the difference of the molecular valency

Table 1. Valency calculation of bond angles of excited and ionised states of molecules.

Molecule	Electronic configuration ^a	State	Bond angle	
			Present method	ab initio ^b
CH ₂ ⁺	(3a ₁) ¹	² A ₁	140	141
CH ₂	(3a ₁) ¹ (1b ₁) ¹	³ B ₁	140	132 (134)
	(3a ₁) ²	¹ A ₁	100	101 (102)
CH ₂ ⁻	(3a ₁) ² (1b ₁) ¹	² B ₁	100	104
	(3a ₁) ¹ (1b ₁) ²	² A ₁	140	131
NH ₂ ⁺	(3a ₁) ²	¹ A ₁	130	120
	(3a ₁) ¹ (1b ₁) ¹	¹ B ₁	180	180
	(3a ₁) ¹ (1b ₁) ¹	³ B ₁	140	140
NH ₂	(3a ₁) ² (1b ₁) ¹	² B ₁	100	103 (103)
	(3a ₁) ¹ (1b ₁) ²	² A ₁	140	143 (144)
	(3a ₁) ² (1b ₁) ²	² B ₂ ^c	60	48
	(3a ₁) ² (1b ₁) ¹	² B ₁	100	111 (112)
H ₂ O ⁺	(3a ₁) ¹ (1b ₁) ²	² A ₁	180	180
	(3a ₁) ² (1b ₁) ²	² B ₂ ^c	50	55
	(3a ₁) ² (1b ₁) ¹	² B ₁	100	111 (112)
HCN	(1a'') ¹ (7a') ¹	¹ ³ A''	130	123 (125)
	(1a'') ¹ (7a') ⁰ (2a'') ¹	¹ ³ A'	160	160 ^d
HCN ⁻	(1a'') ² (7a') ¹	² A'	140	130

^aThe inner electronic configurations (1a₁)² (2a₁)² (1b₂)² for AH₂ type molecules and (1a')² (2a')² (3a')² (4a')² (5a')² (6a')² for HCN are omitted;

^bMulliken and Ermler (1981); values in parenthesis are experimental;

^cone electron missing from 1b₂;

^dSchwenzer *et al* (1974).

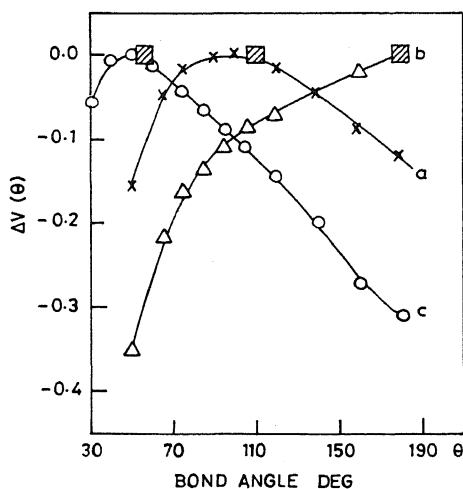


Figure 1. Plots of $\Delta V(\theta)$ versus (θ) for (a) ²B₁ (b) ²A₁ (c) ²B₂ states of H₂O⁺. See table 1 for the electronic configurations of these states. ▨ denotes the equilibrium bond angles found by *ab initio* methods.

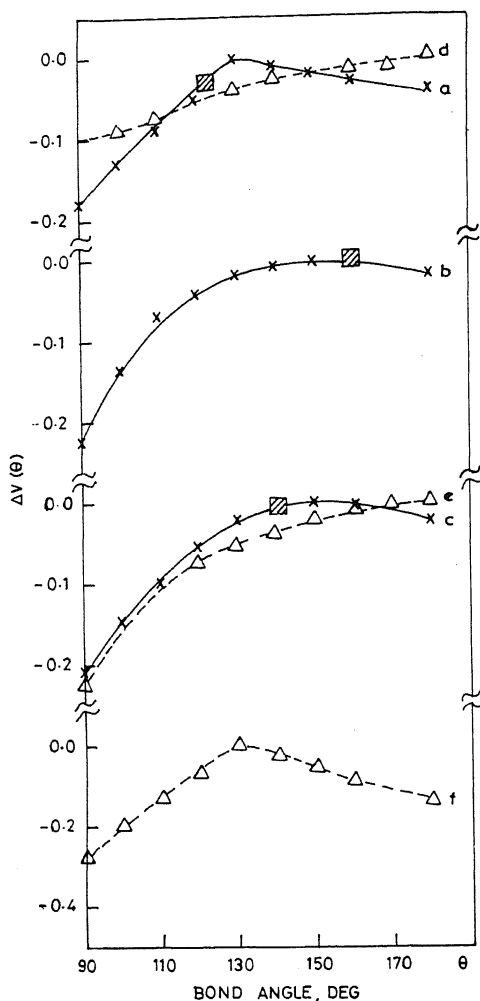


Figure 2. Plots of $\Delta V(\theta)$ versus θ for (a) $1^3A''$ (b) $1^3A'$ (c) $2^2A'$ (d) $2^3A'$ (e) $2^3A''$ (f) $3^3A'$ states of HCN. Full lines indicate present valency results for states already studied while broken lines are for as yet unknown states. See tables 1 and 2 respectively for the electronic configuration of these states. $\blacksquare$ denotes the equilibrium bond angle calculated by *ab initio* methods.

at a particular bond angle from the maximum value, i.e. $V_M(\theta) - V_M^{\max}$ versus θ , to give an idea of the change in molecular valency with bond angle. These are given in figures 1 and 2 for various excited and ionised states of H_2O and HCN as two typical cases.

It is clear from table 1 and figures 1 and 2 that for all the molecules presently studied, valency predictions compare reasonably well with the reported values. In fact, the agreement may be said to be very good when we take into account the simplicity of our method, in contrast to the other more sophisticated but time-consuming methods involving extensive CI. What is remarkable is that even very acute angles such as 55° for the $2B_2$ state of H_2O^+ and 47.5° for the $2B_2$ state of

Table 2. Valency prediction of bond angles of unknown excited and ionised states of molecules.

Molecule	Electronic configuration ^a	State	Bond angle
CH ₂	(2a ₁) ² (1b ₂) ¹ (3a ₁) ² (1b ₁) ¹	³ A ₂	50
	(2a ₁) ² (1b ₂) ¹ (3a ₁) ¹ (1b ₁) ²	³ B ₂	45
	(2a ₁) ¹ (1b ₂) ² (3a ₁) ² (1b ₁) ¹	³ B ₁	90
	(2a ₁) ¹ (1b ₂) ² (3a ₁) ¹ (1b ₁) ²	³ A ₁	180
H ₂ O ⁺	(2a ₁) ¹ (1b ₂) ² (3a ₁) ² (1b ₁) ²	² A ₁	85
HCN	(5a') ² (6a') ¹ (1a'') ² (8a') ¹	² ³ A'	180
	(5a') ² (6a') ² (1a'') ¹ (8a') ¹	² ³ A''	180
	(5a') ¹ (6a') ² (1a'') ² (7a') ¹	³ ³ A'	130

^aInner electronic configurations (1a₁)² for CH₂ and H₂O⁺ and (1a')² (2a')² (3a')² (4a')² for HCN are omitted.

NH₂ are reproduced fairly well by the present method, which gives values of 50° and 60°, respectively. Our method also distinguishes correctly between the singlet and triplet states of the same electronic configurations (for example the ¹B₁ and ³B₁ states of NH₂⁺ – see table 1).

We have also predicted bond angles of some as yet unknown excited states. These are given in table 2 and plots of $\Delta V(\theta)$ versus θ for the unknown states of HCN have been included in figure 2. It may be remarked that the linearity or bent nature of these states are what one would predict qualitatively from Walsh's type of arguments (Walsh 1953). However, it should be noted that such arguments cannot quantitatively predict bond angle values.

Theoretical reasons for the surprising success of this simple model are not fully understood. Efforts are under way to establish this method on a firmer footing by examining the basis of Walsh diagrams and the general applicability of MO valency as a quantitative ordinate of Walsh diagrams for excited and ionised states of molecules. Details will be published elsewhere (Siddarth and Gopinathan 1987).

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Metastable lifetimes and fast chemical reactions

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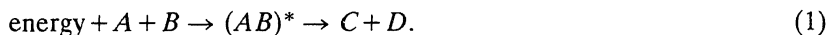
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Abstract. We point out that, using the first-passage time formalism, it is now possible to calculate metastable lifetimes in the limit of the free energy barrier which is *small* compared to thermal energies. This opens the possibility of calculating rates for fast chemical reactions. Possible experimental checks include explosive branching reactions, decreasingly stable molecular series, and bistable molecular isomers.

Keywords. Metastable lifetimes; fast chemical reactions; first-passage time formalism; non-Arrhenius reaction rates.

1. First-passage-time formalism and low-barrier limit

Kramers (1940), motivated by the need to calculate chemical reaction rates, considered the now classic problem of escape of a Brownian particle across a potential barrier in one dimension. The barrier, in chemical language, corresponded to the free energy cost of forming an activated complex, with the energy supplied thermally. The Brownian position variable was some reaction coordinate x (figure 1),



These ideas were generalized to several variables, $x \rightarrow (x_1 \dots x_n)$ by several authors (Brinkman 1956; Landauer and Swanson 1961; Langer 1969) independently. The barrier now becomes a 'saddle' in n dimensions, with a metastable and an unstable well on either side. The Brownian particle jiggles around thermally in the metastable well, and at some time jumps over the saddle on the free energy surface, to the globally stable minimum.

In all dimensions n , the calculation gave an Arrhenius-type expression for the reaction rate R ,

$$R = \omega e^{-\beta \Delta F}, \quad (2)$$

where ω is the attempt frequency, $\beta = (k_B T)^{-1}$ the inverse temperature, and ΔF the free energy difference between the metastable minimum and the saddle point. The Kramers-type calculations involved the assumption of a quasithermal distribution and a slow leakage of probability over the saddle, enabling a calculation of the steady probability current flow, and hence an evaluation of the *rate*. The 'slow-leakage' condition implied a small rate R , and hence a high barrier/low noise condition,

$$\Delta F/k_B T \gg 1 \quad (3)$$

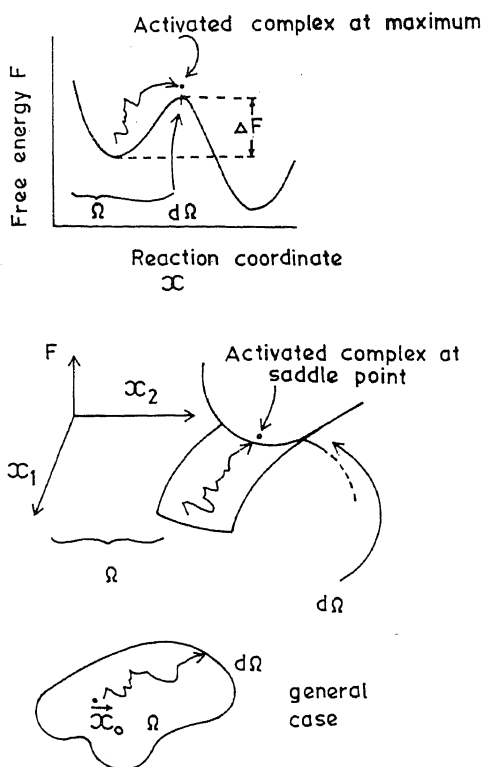


Figure 1. Barrier escape of a Brownian 'particle'.

An alternative formalism, based on conditional probabilities, is the 'first-passage time' formalism (Stratonovich 1963). As the name implies, it involves considering a random variable $\mathbf{x} = (x_1 \dots x_n)$ inside some region Ω (metastable well), placed initially at $x_0 \in \Omega$. The random variable crosses the boundary $\partial\Omega$ in a mean first passage time $T_p(\mathbf{x}_0)$. The formalism expresses the mean first passage time $T_p(\mathbf{x})$ as the solution to a differential equation:

$$L_{\mathbf{x}}^+ T_p(\mathbf{x}) = -1, \quad (4)$$

where

$$L_{\mathbf{x}}^+ = \sum_{i=1}^n D \frac{\partial^2}{\partial x_i^2} - \mathbf{A}_i(\mathbf{x}) \frac{\partial}{\partial x_i}. \quad (5)$$

Here D is the diffusion constant $= C_0 k_B T$ ($C_0 = \text{constant}$), and $\mathbf{A}(\mathbf{x})$ is the deterministic force $\mathbf{A}(\mathbf{x}) = C_0 \nabla_{\mathbf{x}} F(\mathbf{x})$. Thus the free energy surface $F(\mathbf{x})$, containing the metastable minimum in Ω and the saddle point on the boundary $\partial\Omega$, determines the FPT. The boundary condition is $T_p(\mathbf{x} \in \partial\Omega) = 0$, as is physically reasonable: any point starting on the boundary has already 'passed', so the passage time is zero. The passage time calculation is then a boundary value problem, involving the solution of a differential equation.

A calculation of the FPT in n -dimensional yields the Kramers expression (2) (with $\partial\Omega$ suitably defined). This is obtained starting from an *exact* expression for

$T_p(\mathbf{x}_0)$ in terms of a ratio of volume (Ω) to surface ($\partial\Omega$) integrals, and then using the sharp-peaking approximations based on (2) (Schuss and Matkowsky 1979).

The stationary probability $P_0(\mathbf{x})$ satisfies the Fokker-Planck equation $L_{\mathbf{x}}P_0(\mathbf{x}) = \dot{P}_0(\mathbf{x}) = 0$. Thus from (4), the identity $\int d^n x P_0(\mathbf{x}) (L_{\mathbf{x}}^+ T_p(\mathbf{x}) + 1) = 0$ holds exactly. The separation $T_p(\mathbf{x}) = \nu(\mathbf{x}, \mathbf{x}_0) T_p(\mathbf{x}_0)$; $\nu(\mathbf{x}_0, \mathbf{x}_0) = 1$, $\nu(\mathbf{x} \in \partial\Omega; \mathbf{x}_0) = 0$, plus partial integration yields (Schuss and Matkowsky 1979),

$$T_p(\mathbf{x}_0) = \frac{\int_{\Omega} P_0(\mathbf{x}) d^n x}{-\int_{\partial\Omega} d^{n-1} x P_0(\mathbf{x}) D \hat{n} \cdot \nabla_{\mathbf{x}} \nu(\mathbf{x}, \mathbf{x}_0)}, \quad (6)$$

where $\hat{n}$ is the outward normal to the boundary $\partial\Omega$. Since $P_0(\mathbf{x}) = \exp[-\beta F(\mathbf{x})]$, sharp-peaking assumptions, for $\Delta F/k_B T \gg 1$ yield (2), with ω in terms of the free energy curvature matrix at the metastable minimum. The function ν is a solution of $L^+ \nu \approx 0$, and can be evaluated in a systematic expansion in $k_B T/\Delta F$. For the one-dimensional case (Gilmore 1979), (4) is exactly soluble, and one can examine the opposite *low barrier/high noise* limit (Agarwal and Shenoy 1981),

$$\Delta F/k_B T \ll 1. \quad (7)$$

One finds that if μ is some control parameter that shrinks the barrier $\Delta F(\mu)$ to zero at some $\mu = \mu_c$, $\Delta F(\mu_c) = 0$, then the FPT varies as a *power* of the barrier, or of the control parameter difference, $\mu - \mu_c$. Thus

$$T_p \sim [\Delta F(\mu)]^{\text{power}} \sim (\mu - \mu_c) \theta_p, \quad (8)$$

where the exponent θ_p in the one-dimensional case is $\theta_p = \frac{1}{2}$ (Agarwal and Shenoy 1981).

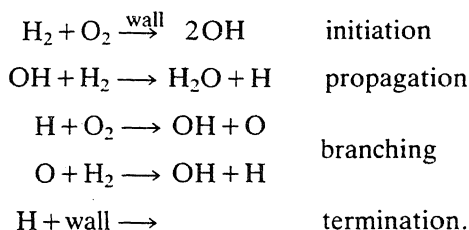
Since (6) is *exact*, one can handle the low-barrier/high-noise limit (7) for a *general* dimension n of the reaction coordinate space (Shenoy 1984) with θ_p depending on the nature of the free energy surface and boundary $\partial\Omega$ defined (nature of reactants and activated complex). This means that *fast* chemical reaction times can in principle be handled if the free energy surface is known. [For a two-mode ring laser (Shenoy and Agarwal 1984), $n = 4$ and one finds $\theta_p = 2$. This has been verified by Monte Carlo simulations (Murthy and Shenoy 1986, unpublished) confirming the formalism].

Of course the control parameter μ that shrinks the barrier is more easily obtained in examples from physics (pressure, temperature, laser pump parameter for saturable absorber). By varying μ rapidly enough, one can prepare a non-equilibrium population in the metastable well, and watch it decay. It is this preparation of the metastable state and possibility of a first-order phase transition which is the problem, in the chemical case. But one can find some possible chemical examples where these ideas can be tested and short reaction times predicted.

2. Possible chemical examples

2.1 Explosive branching reactions

Hydrogen and oxygen, under high temperatures and pressures, undergo a chain of reactions (Alberty 1983).



The branching reaction is explosive, for a range of temperatures and pressures. Figure 2 gives a rough 'Phase diagram', with rapid reactions occurring as the boundary is crossed. Thus, at $T = 550^\circ\text{C}$ for $P < 100$ Pa the reaction is slow, while for $P = 100$ Pa the reaction is fast. Similarly for $P > 1.33 \times 10^4$ Pa it is slow while for $P = 1.3 \times 10^4$ Pa it is fast.

Since one has a parameter (in fact, two) to control ΔF , that shrinks at the boundary, one could in principle calculate reaction rates close to the boundary, given a knowledge of the hydrogen-oxygen atom free-energy surface.

2.2 Decreasingly stable molecular series

The basic problem, as stated, is to have some method of decreasing the free-energy barrier for the decay of a metastable state.

One could take a metastable molecule, and excite it by a laser, say to decreasingly stable molecular levels, measuring the decay times from the (increasingly) excited states (see figure 3a). The control μ is the laser frequency. If the energy surface in three dimensions is known, e.g., by quantum mechanical calculation, and if the decay is classical (no tunnelling-through), then the low-barrier decay time could be calculated.

Alternatively, one could consider decreasingly stable molecular series, prepared separately, with known (decreasing) activation barriers for dissociation (figure 3b). The control parameter μ is the molecular tailoring. The dissociation time could be measured and compared with theory.

2.3 Bistable molecular isomers

Molecular isomers are known, where two distinct forms have the same energy, with a barrier to the deformation of any isomer into another.

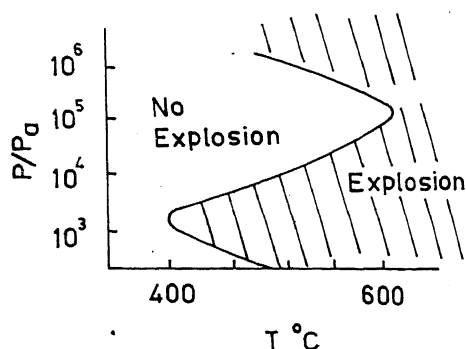


Figure 2. Pressure versus temperature stability diagram for hydrogen and oxygen.

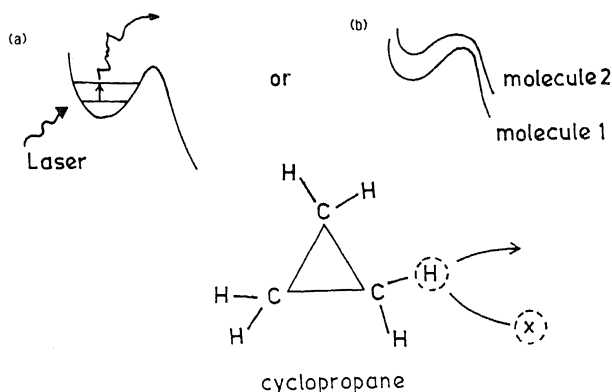


Figure 3. Effective barrier lowering through excitation.

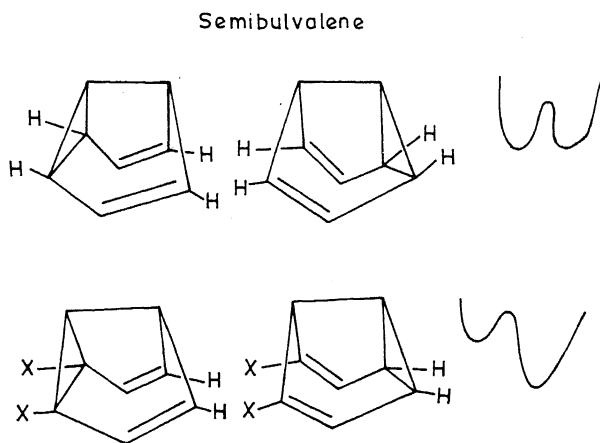


Figure 4. Asymmetric barriers by substitution.

(i) Semi-bulvalene is an example (figure 4), with hydrogen atoms attached to an organic ring with bonds connecting the points of attachment. One can replace the hydrogen by a complex X that strains this configuration, so that the two configurations shown (figure 4) have different energies, and a reduced free energy barrier ΔF . $\Delta F \sim 5$ kcal/mole (say) ~ 0.2 eV, corresponding to $\Delta F/k_B T \sim 8$. This is still high but with judicious 'doping of the molecule, if one were to get $\Delta F/k_B T < 1$, one might be in the power-law regime of decay times.

One could prepare the non-equilibrium populations in the metastable well by laser irradiation at a frequency destroying the major (more stable) molecular species.

Alternatively, one could add the complex X to replace the H, and cool suddenly. If the reaction adding X proceeds faster than the hop-over, one will have a non-equilibrium 50-50 population of the X-compound, that will then decay to the unequal fractions dictated by the thermodynamics.

(ii) Acetaldehyde is another example, existing in the two states shown in figure 5. The unequal reaction rates indicated by the arrows imply that the free energy

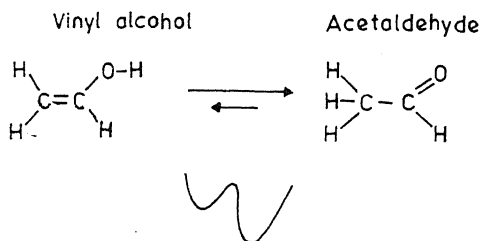
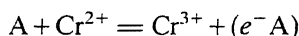


Figure 5. Asymmetric barriers in isomers.

barrier is asymmetric. The required non-equilibrium population could be created by laser pulses at frequencies that suddenly destroy the single C–C bond, leaving a non-equilibrium molecular form as dominant.

2.4 Electron transfer reactions

These involve electron pull-offs like



and would cost, in terms of energy, typically of the order of 0.1–1 eV. One might think of the capturing molecule A as a film on an anode in a solution with Cr^{2+} ions. The barrier might conceivably be reduced by the applied voltage.

3. Conclusions

In conclusion, fast metastable decay times can in principle be calculated by recent formal developments. The problem is then to find chemical examples where a non-equilibrium population can be prepared in a metastable well with a free-energy barrier that is small compared to thermal energies. Some examples have been suggested. More work on the application of these ideas would clearly be worthwhile.

Acknowledgements

It is a pleasure to acknowledge generous discussions, regarding possible chemical examples, with E D Jemmis, K D Sen, M Durga Prasad, R Ramaswamy, and B L Tembe.

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The fragment molecular orbital approach in organometallic reactivity. Reactions of the binuclear complexes

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Abstract. The fragment molecular orbital approach has emerged as a framework model in theoretical organometallic chemistry. This provides an understanding of the electronic structure and bonding in polynuclear complexes in terms of their constituent fragments that are well understood. Symmetry properties of the frontier molecular orbitals of organometallic complexes help in explaining their reactivity towards various reagents.

Keywords. Fragment molecular orbitals; reactivity in organometallics.

1. Introduction

Modern transition metal organometallic chemistry defies most attempts at prediction. With the experimental facilities at his disposal the organometallic chemist generates a bewildering array of complexes (Wilkinson *et al* 1982; Yamamoto 1986). Whether these are products of planned syntheses or fall-outs from totally unexpected conditions, nature has taken its course. It is left to the chemist to develop a model based on the available information for understanding the structure and bonding of these complexes and the reactions leading to them. After a measure of success is achieved in explaining the observations, predictions can be attempted based on the same model. Here we present a brief introduction to the fragment molecular orbital approach, which is a reasonably successful model for understanding the structural preferences of transition metal organometallic complexes (Hoffmann 1981). Reactivity presents a more formidable problem. Examples of the theoretical studies of the reactivity of binuclear complexes leading to new C-C bonds will be discussed based on the fragment molecular orbital approach.

2. The fragment molecular orbital approach

In this approach the molecule is divided into smaller fragments that can be understood easily. The variations in the energy levels and wavefunctions of the fragments as a result of the reconstruction of the molecule provide valuable insights. Such a method has been used frequently in organic chemistry (Jorgensen and Salem 1973). It is ideal in organometallic chemistry where the fragmentation only separates the organic and metal parts. An ever-expanding library of the

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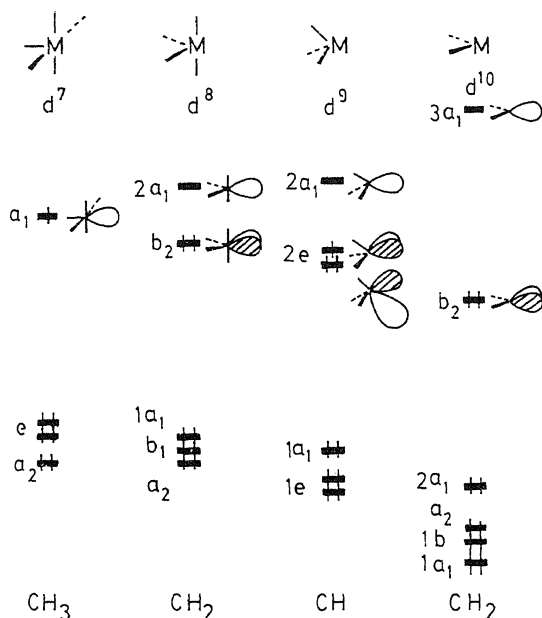
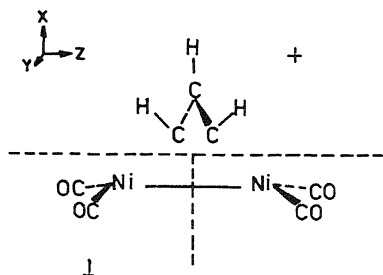


Figure 1. The frontier orbitals of ML_5 , ML_4 , ML_3 , and ML_2 fragments and their isolobal organic equivalents.

molecular orbitals of such fragments are available (Albright *et al* 1985). These can be constructed logically starting from the molecular orbitals of a transition metal complex. Figure 1 shows the frontier orbitals of a general octahedral complex and the fragments ML_5 , ML_4 , ML_3 , and ML_2 (Jemmis and Hoffmann 1980). The variation of the energy levels as a function of the structure of these fragments is studied in detail. The basic splitting of the d orbitals in an octahedral field and the decrease in energy of metal based orbitals on removing each ligand justify these orbital patterns. From a valence bond point of view the removal of a ligand leaves a directed orbital at the metal. When there are more than one such orbital the appropriate symmetry-adapted linear combinations are shown. Even though the details vary with the ligand, the general pattern of orbitals is independent of them. The use of the fragment approach is not restricted to these small fragments. If a fragment, however large it may be, appears as a common part in many complexes it is profitable to analyse the electronic structure in terms of the fragment molecular orbitals of the larger fragment (Hoffmann 1981).

Just like the building-up of complicated organic molecules from smaller fragments such as CH_3 , CH_2 , CH and C , that of larger stable organometallic complexes may be envisaged by putting together the ML_n fragments with appropriate organic groups. The advantage of such a treatment has been amply demonstrated. Thus the interaction of a d^7 ML_5 fragment, say $Mn(CO)_5$ with CH_3 gives $Mn(CO)_5CH_3$ with an $Mn-C$ σ bond. Two of these fragments could give $(OC)_5Mn-Mn(CO)_5$ with an $M-M$ σ bond.

A somewhat more complex example is shown in some detail. Derivatives of $(OC)_2Ni(\mu-C_3H_3)Ni(CO)_2^+$, **1** are shown to possess a C_{2v} structure where the C_3H_3 group straddles the $M-M$ bond (Jeffery *et al* 1981; Jemmis and Prasad



1987b). Let us see how the fragment molecular orbital approach helps in understanding the factors that hold this molecule together. The obvious way of dissecting this molecule is into $(\text{CO})_4\text{Ni}_2$ and C_3H_3^+ groups. The $(\text{CO})_4\text{Ni}_2$ can be further divided into the two $\text{Ni}(\text{CO})_2$ groups. The $d^{10}\text{ML}_2$ fragment has a LUMO a_1 (mostly a $4s$, $4p$ hybrid) and a HOMO b_2 (mostly d_{xy} in the coordinate system shown in 1). The remaining metal orbitals lie much lower in energy. When two $\text{Ni}(\text{CO})_2$ groups are brought together the frontier orbitals obtained are the bonding combinations of the sp hybrid and the two π type orbitals arising from the $b_2(d_{xy})$ orbital (figure 2). The lower-lying occupied orbitals do not play much of a role in binding the C_3H_3 unit. The frontier orbitals of the C_3H_3 group can be obtained starting from the well-known allyl cation. Removing two hydrogens from the allyl cation leaves the bonding and anti-bonding combination of the hybrid orbitals. The non-bonding π MO is also within the bonding range in relation to the metal fragment. Since there are three orbitals of matching symmetry in $\text{Ni}_2(\text{CO})_4$ and the number of electrons involved, six, is sufficient to occupy the three bonding combinations the structure is stable (Jemmis and Hoffmann 1980; Jemmis and Prasad 1987b).

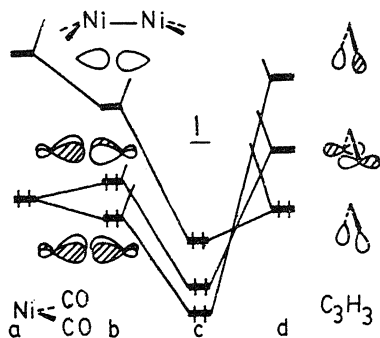


Figure 2. The construction of frontier orbitals of $(\text{CO})_2\text{Ni}(\mu\text{-C}_3\text{H}_3)\text{Ni}(\text{CO})_2^+$, 1. (a) The frontier molecular orbitals of $\text{Ni}(\text{CO})_2$ (cf. figure 1). (b) Only three frontier orbitals result from the interaction of two $\text{Ni}(\text{CO})_2$ fragments. (c) This represents the 3 pairs of $2e-2$ orbital interactions leading to the stable structure 1. (d) The nonbonding π and the σ and σ^* combinations of the didehydroallyl cation.

3. Isolobal analogy

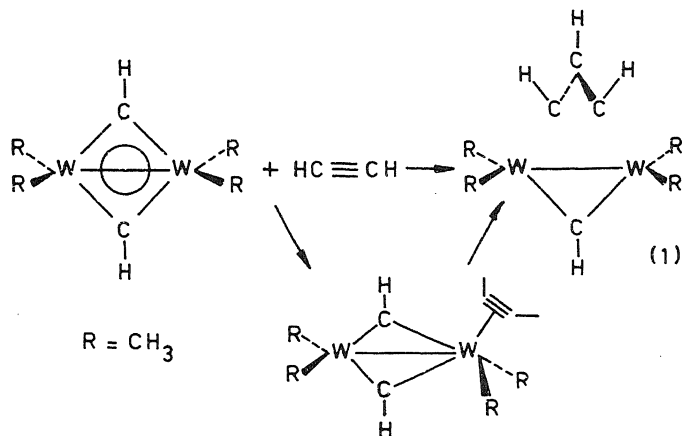
Often the concept of isolobal analogy is employed for comparison of the organometallic complexes with the familiar organic compounds. Two groups are termed as isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar (Hoffmann 1982). The various ML_n fragments in figure 1 are then isolobal to CH_3 , CH_2 , CH . This enables us to predict the organometallic equivalents of cyclobutane, tetrahedrane and the like. All these enable us to look at the electronic structure and bonding in organometallic complexes in comparison to those of the organic counterparts. With a series of replacements the $Ni_2(CO)_4(\mu-C_3H_3)^+$, 1, discussed above can be shown to be the organometallic equivalent of cyclopentenyl cation (Jemmis and Prasad 1987b). What can be said about reactions involving organometallic compounds?

4. The fragment molecular orbital approach to reactivity

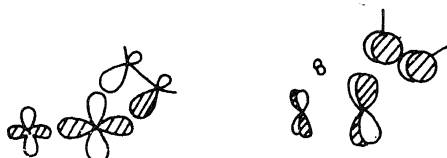
In principle the potential energy hypersurface for a given assembly of atoms can be studied theoretically. In practice however, only the smallest of these can be done currently with the desired accuracy. Theoretical methods at various levels of approximation have been applied to study reactions of organometallic compounds. A survey of the theoretical study of the various reactions involving C-C bond formation at mononuclear complexes shows that just about all theoretical methods available for calculation of the electronic structure of molecules have been employed. These include the Extended Hückel method, various modifications of the semiempirical SCF methods, the non-empirical Fenske-Hall, *ab initio* SCFMO with CI, and the Generalized Valence Bond method. The reactions studied are methyl migration or carbonyl insertion (Koga and Morokuma 1986), olefin metathesis (Rappe and Goddard 1982), ethylene coupling (Steigerwald and Goddard 1985), Ziegler-Natta catalysis (McKinney 1980), oxidative addition and reductive elimination (Low and Goddard 1986), and double carbonylation (Tatsumi *et al* 1986).

A common observation in all of them is that at the end of even the most sophisticated study, numerical predictions cannot be made with a high degree of accuracy, and hence, the results are analysed in terms of qualitative concepts. This may remain so for some time to come.

There are a few studies of the reactions of binuclear and polynuclear complexes (Hoffmann *et al* 1978). The concept based on perturbation theory and symmetry developed for organic reactions (Woodward and Hoffmann 1971; Fukui 1975; Fleming 1976; Klopman 1974) can be profitably extended to the transition metal complexes. Such extensions are not very straightforward due to the increased number of variables present. Each set of reactants has to be analysed as a separate problem for some time to come. With the experience gained from a series of such studies, generalizations that are widely applicable should emerge. We shall now present an example where a fragment molecular orbital approach based on a qualitative wavefunction provided useful insight into an organometallic reaction (1) (Jemmis and Prasad 1987a). The substituents on the carbons are shown as



hydrogens for simplicity. The following points may be noted about this reaction. Among the two $\mu\text{-CH}$ groups only one group reacts even if an excess of acetylene is used. Reaction is facile with acetylene or allene but does not proceed with ethylene or butadiene. Isostructural Ta and Nb complexes which have two electrons less do not react with alkynes under the same condition. An intermediate acetylene π complex has been isolated and characterized during this reaction. A fragment molecular orbital analysis showed that the HOMO is a metal-metal σ bond and LUMO is δ^* in character. Distortion of this compound to a geometry appropriate to those found in the intermediate acetylene complex localizes the HOMO and LUMO to the pyramidalized metal. This facilitates the donor acceptor interactions shown in 2.



2

Since these involve a μ donor orbital in one plane and a μ acceptor orbital in a perpendicular plane of the organic group, only molecules with μ orbitals in perpendicular planes will react. Thus alkynes, allene, CO, HCN, HNC etc. but not butadiene and ethylene are expected to react. The reaction may not proceed if two electrons that form the M-M bond are not available for donation. This happens in Nb and Ta complexes. There is already an incipient bonding between the intermediate acetylene complex which proceeds to form the product with a bridging C_3H_3 group. A comparison of the LUMO of $(\text{CH}_3)_2\text{W}(\mu\text{-CH})_2\text{W}(\text{CH}_3)_2$ and the final complex explains the absence of reactivity of the $\mu\text{-CH}$ group of the final complex with excess acetylene. The replacement of the CH group by C_3H_3 brings in the nonbonding π orbital of a_2 symmetry. This orbital, occupied in the current electron count, has the right symmetry for interaction with the δ^* orbital pushing it from the bonding range. Hence acceptance of electrons from the acetylene is not possible, thus preventing the reaction (Prasad *et al* 1986).

The fragment molecular orbital approach has recently been applied to study the reactivity of $[\text{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-L})(\text{L} = \text{CO}, \text{CH}_2, \text{C} = \text{CH}_2, \text{CH}^+)$ (Bursten and Cayton 1986). Here two CpFe(CO) units are brought together. This is interacted with one bridging carbonyl. The resultant $[\text{CpFe(CO)}]_2(\mu\text{-CO})$ group has been combined with various second-bridging substituents. The photochemical reactions of the doubly-bridged complexes are shown to be LUMO-controlled. Protonation of the complex is shown to be controlled by the nature of the bridging ligands. It is charge controlled when $\text{L} = \text{CH}_2$ but orbital controlled when $\text{L} = \text{CO}$. We feel that there is a lot to be gained by such studies of polynuclear systems.

5. Conclusions

A fragment molecular orbital approach where a molecule is schematically dissected into small fragments which are well-understood helps in understanding the electronic structure and bonding of transition metal organometallic complexes. This is demonstrated for $(\text{OC})_2\text{Ni}(\mu\text{-C}_3\text{H}_3)\text{Ni(CO)}^+$. Theoretical studies of the reactions of transition metal complexes are more difficult and less common. Symmetry and overlap-based arguments may be applied for explaining and predicting reactivity in specific cases. The reaction of $\text{L}_2\text{W}(\mu\text{-CR})_2\text{WL}_2$ with acetylene is given as an example.

Acknowledgements

The University Grants Commission is thanked for financial assistance.

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Molecular electrostatic potential mapping using a dipole

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Abstract. A new method of mapping molecular electrostatic potentials using a dipole of arbitrary length and strength has been developed. The dipole is allowed to move on a geometrical surface enclosing the molecule under study such that the closest distance of approach (CDA) between the two species is fixed. Potential maps of water, formaldehyde and ethylene epoxide molecules have been studied by this approach for CDA values of 2 and 5 Å. Experimental geometries for the molecules and net charge distributions obtained by the MNDO molecular orbital method were used in the calculations. Dipole potential maps obtained by the present method are compared with those obtained by the prevalent monopole mapping method. The two approaches broadly predict the same sites for potential minima in the molecules studied. The present dipole maps are however more informative, especially with regard to electric field directions, than the monopole maps, and it has been shown that this additional information is very useful.

Keywords. Electrostatic potential mapping; dipole potential mapping; molecular electric fields.

1. Introduction

Molecular electrostatic potential maps provide useful clues to favoured modes of interactions of molecules. It is particularly useful for studying biomolecular recognition where due to the large size of molecules involved, adequate molecular orbital treatments become cumbersome (Del Re *et al* 1985). A positive monopole is employed as the mapping device in the prevalent method of potential mapping (Scrocco and Tomasi 1978). As a monopole has no spatial extension and orientational capability, it cannot generally represent a molecule. Thus monopole potential maps yield no information on preferred orientations of two interacting molecules and probable hydrogen-bonding directions. Magnitudes of monopole potential energies are also generally too high to correspond to real intermolecular interactions. These considerations suggest that alternative methods of potential mapping need to be developed. As biomolecular recognition is essentially a long range interaction process where two molecules would mainly influence each other via the dipole-dipole interaction mechanism, a dipole was considered to be a suitable mapping device and used in the present approach.

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2. Method of calculation

The electrostatic interaction energy of a given dipole with a molecule may be evaluated using either the multipole interaction scheme or interactions of the net charges directly (Gray and Gubbins 1984; Price *et al* 1984). Our computer program includes both these possibilities as options. A comparative evaluation of the two approaches (Mishra and Tewari 1986) does not show any noticeable superiority of the multipole formalism over that based on direct interactions of the net charges, though calculations using the multipole approach are generally more complex. Therefore, the potential energies of interaction of the molecules studied here were calculated using a mapping dipole of length 1 Å and strength 1 Debye, and not charge-charge interactions. Experimentally determined geometries (Callomon *et al* 1976) of the molecules were employed and net charge distributions used were obtained with the MNDO molecular orbital method (Dewar and Thiel 1977). Two closest distances of approach (CDA) i.e. 2 and 5 Å, between the mapping dipole and the molecules in question were used. At each chosen point on the CDA surfaces, the mapping dipole was allowed to orient itself along the direction of minimum interaction energy; these energies were taken as characteristic potentials of the corresponding points. It is obvious that the present method of potential mapping has one aspect common with electric field mapping i.e. the direction of the mapping dipole. But while in electric field mapping the quantity evaluated is the electric field, in the present approach the potential energy of electrostatic interaction between a molecule and the dipole is calculated. In other words, the present method yields information with regard to potential and electric field direction simultaneously. In order to compare the present results with those of monopole mapping, monopole potential maps for the molecules studied here were also obtained using the QCPE program no. 249 using the same net charges and geometries as mentioned above; the contours were obtained via a line printer and then redrawn manually. This limits the degree of smoothness of the contours but the potential features can still be easily extracted.

3. Results and discussion

Potential maps for three molecules: water, formaldehyde and ethylene epoxide, are presented in figures 1a and 1b to 3a and 3b, respectively. The "a" parts of the figures contain dipole potential maps obtained by the present approach whereas the "b" parts contain the corresponding monopole potential maps. In the dipole maps, potential distributions are presented with the help of certain chosen points in each case; potentials at the other points can be obtained approximately by interpolation. The monopole potentials are presented as isopotential contours. The numbers given in the dipole potential maps are potential energies in the unit of 0.1 kcal/mole; the arrows in these maps correspond to electric field directions at the corresponding points. The numbers given in the monopole potential maps are potential energies in kcal/mole. These maps exhibit the following features.

According to figure 1a, there is a fairly extended region of potential minimum near the oxygen atom of the molecule of water on the exterior side of the HOH angle. Another shallow potential minimum exists in the middle of the interior

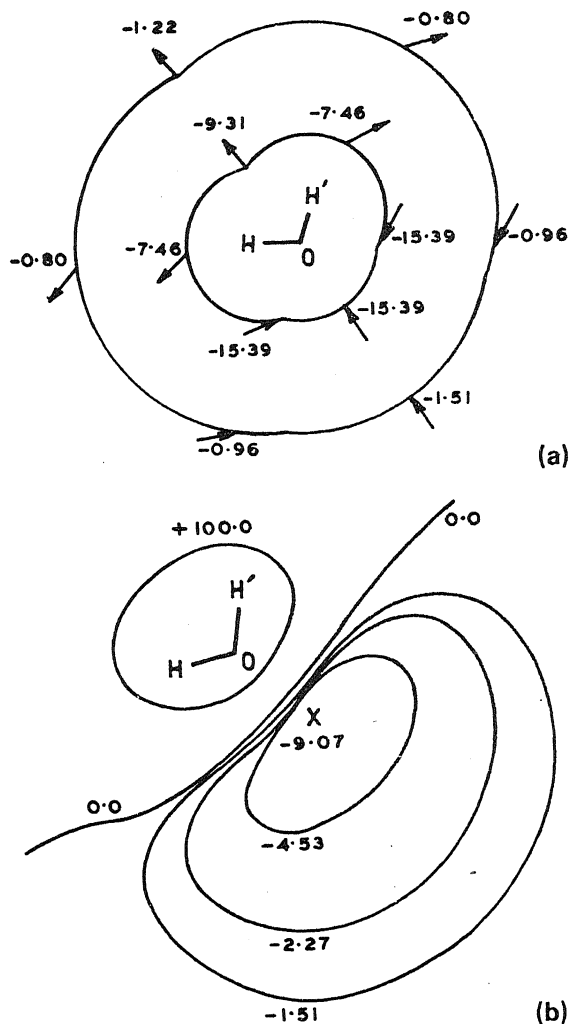


Figure 1. Dipole (a) and monopole (b) potential maps of water in molecular plane.

HOH angle also. These observations are broadly valid for both the 2 and 5 Å CDA surfaces. As *ab initio* net atomic charges are significantly larger in magnitude (Hankins *et al* 1970) than those obtained by the MNDO method, use of the former in place of the latter would result in larger magnitudes of potential energies. However, it would not significantly affect the main potential features and electric field directions especially for symmetric molecules like water. The monopole potential map presented in figure 1b also shows the minimum near the oxygen atom of water on the exterior side of the HOH angle (Scrocco and Tomasi 1978). Thus the maps of figures 1a and 1b broadly agree with regard to the location of the potential minimum. The map of figure 1a has an important additional information in comparison to that of figure 1b i.e. with regard to the directions of electric field at the various points. The importance of the electric field directions would become clear from the following discussion.

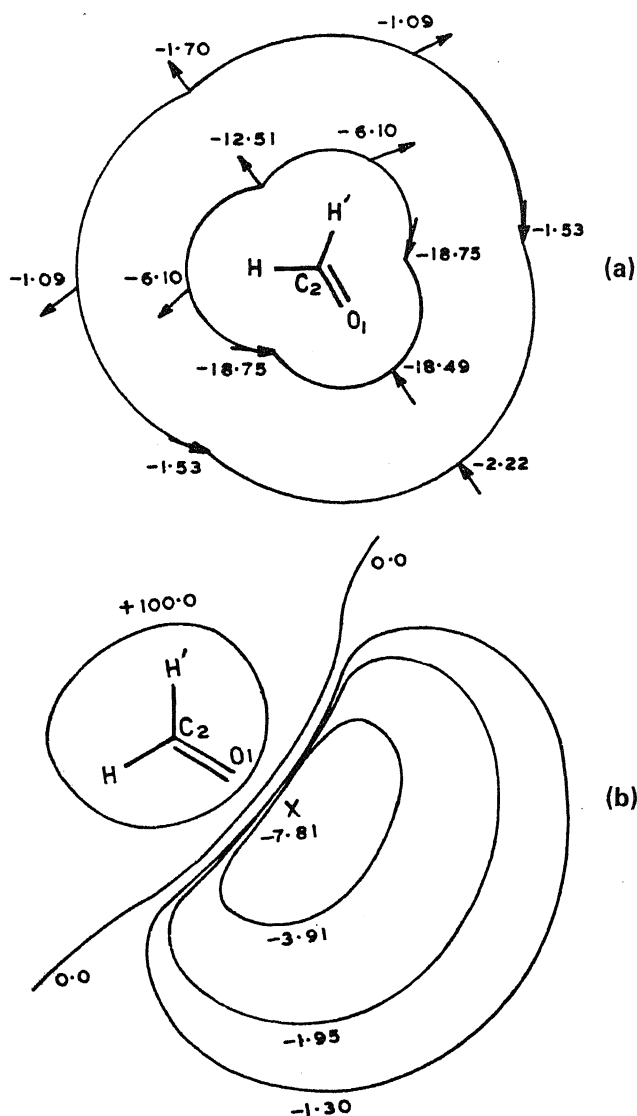


Figure 2. Dipole (a) and monopole (b) potential maps of formaldehyde in the molecular plane.

Let us consider the hydrogen-bonded dimer of water. This aspect has been discussed in the literature in several reviews and papers (Rao 1972; Hankins *et al* 1970). Thus out of the three hydrogen-bonded configurations for the water dimer—the so-called linear, cyclic and bifurcated—the linear one, having a plane of symmetry and the non-bonded protons of the monomers being *trans* to each other, has been found to be the most stable. The angle of rotation of the OHO plane of the second water molecule with respect to the OH bond of the first has been shown to be 40° (Hankins *et al* 1970). Our results presented in figure 1a show that the electric field when observed in the OH bond directions near the hydrogens is

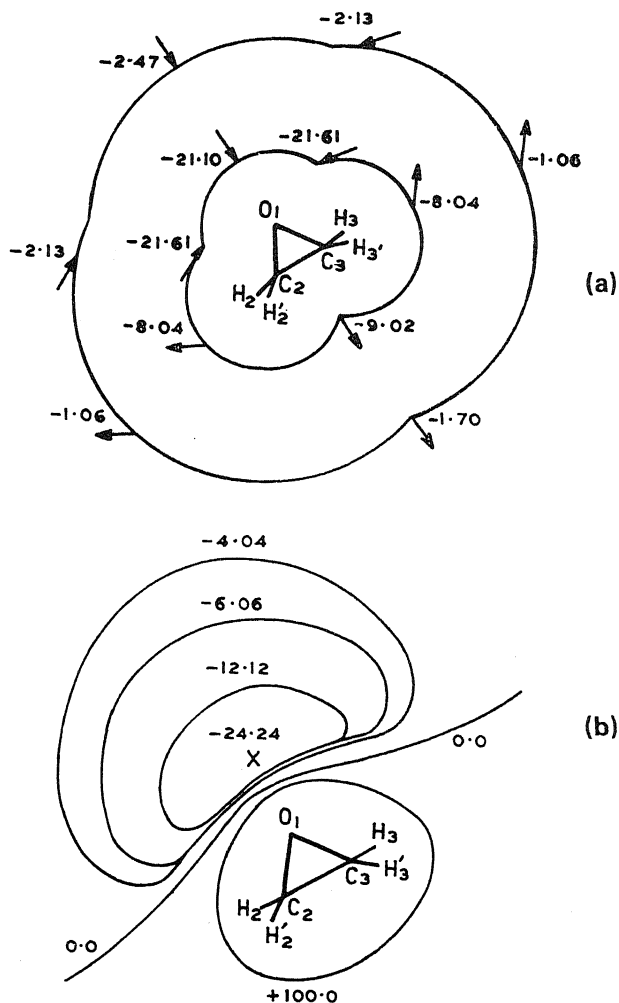


Figure 3. Dipole (a) and monopole (b) potential maps of ethylene oxide in the OCC plane.

inclined at about 30° with respect to the bonds. It is further noted that in going from one to the other CDA surfaces the electric field direction remains almost constant in a given region of the molecular space. Thus even on the basis of electric field considerations alone, one can predict the relative orientations of the two water molecules in the linear dimer with reasonable accuracy. Similarly, for the other two hydrogen-bonded configurations also, relative molecular orientations are satisfactorily predicted by the map of figure 1a. Obviously the monopole potential map of figure 1b completely fails in making predictions of this kind. It should be mentioned that despite the success of the present approach in elucidating molecular electrostatic potential and electric field features successfully, it cannot generally be used to predict relative stabilities of different hydrogen-bonded configurations. This is because in addition to electrostatic interactions, other interactions e.g.

charge transfer, polarization and overlap etc. which are not included in the present approach also contribute, more or less, to hydrogen bonds. Further, the contributions of these interactions and optimal interatomic distances, which may not be known, would be different in different configurations.

Dipole and monopole potential maps of formaldehyde are presented in figures 2a and 2b. According to figure 2a, broadly speaking, the minimum potential energy region in formaldehyde lies around the oxygen atom and is quite extended. At the 2 Å CDA surface, the potential in front of the CO bond of formaldehyde is about 0.03 kcal/mole higher than that of the minimum which is located almost in front of the HC bond. At the 5 Å CDA surface, the minimum is located in front of the CO bond. Figure 2b also shows the potential minimum, as detected by a positive monopole, as located near the oxygen atom (Scrocco and Tomasi 1978). Thus the potential maps of figures 2a and 2b are broadly in agreement.

The dipole potential map of ethylene epoxide in the plane containing the carbon and oxygen atoms is presented in figure 3a. It has features similar to those of figure 2a. The maps of figures 3a and 3b broadly agree in that the potential minimum in ethylene epoxide lies near the oxygen atom. The monopole potential map of this molecule has been studied by Politzer *et al* (1978) using an *ab initio* approach. The maps presented in the figures 3a and 3b are in agreement with those due to these authors with regard to the location of the potential minimum. It may be remarked that ethylene epoxide, in particular some of its derivatives, are known to be carcinogenic.

Electric field directions in the maps of figures 1a, 2a and 3a are very similar together. This is not surprising as the three molecules belong to the same point group.

Acknowledgement

The work was partly supported by a project grant from UGC, New Delhi, for which PCM is thankful.

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Nucleoside antibiotics: Conformation and biological activity

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Abstract. Minor modifications in pyrimidine and purine nucleosides have a profound effect on their biological activity. These modified nucleosides which exhibit a wide variety of antiviral, antibacterial, antitumor or cancerostatic properties are collectively called as nucleoside antibiotics. Conformational properties of these antibiotics have been investigated by quantum mechanical PCILO method. The results indicate that the nucleoside antibiotics and their parent nucleosides have very similar conformational preferences and this is specially so in the situations that occur in aqueous media. This result has important biological implications: these antibiotics can easily get incorporated in growing chains of RNA or DNA by mimicking their parent nucleosides and then bring about the inhibition of RNA or DNA or protein synthesis.

Keywords. Nucleoside antibiotics; conformation; biological activity; PCILO; modified nucleosides.

1. Introduction

Nucleoside antibiotics constitute a class of biologically active compounds which result from minor modifications or substitutions in the pyrimidine and purine nucleosides. The modifications can occur either in the sugar ring or in the base. As a result of this, nucleoside antibiotics exhibit a wide variety of antibacterial, antiviral, antitumor and cancerostatic properties (Bloch 1975a). Quite a few of these antibiotics have been tested clinically on animals and humans in a bid to search for a potential drug against cancer and viral diseases (Bloch 1975b).

Examples of sugar-ring modifications are shown in figure 1. In arabinosyl nucleosides (figure 1a), the 2'-hydroxyl group is on the same side as that of the C5' and on opposite side as that of the 3'-hydroxyl group. The base can be either adenine or cytosine and the resulting modified nucleosides: Ara-A and Ara-C are both cytotoxic agents. Both of them have been extensively studied as inhibitors of mammalian cells in culture, tumor cells and viruses. They get phosphorylated and incorporated as terminal residues into DNA *in vitro*. Ara-A gets incorporated into the 3'-terminal end of tRNA (Suhadolnik 1970, 1979). The replacement of 3'-hydroxyl group in adenosine by a proton and an amino group results in 3'-deoxy adenosine (cordycepin) and 3'-amino-3'-deoxy adenosine (figure 1b), respectively. Cordycepin is a cytostatic agent and a strong inhibitor of RNA polymerase. 3'-amino-3'-deoxyadenosine exhibits antitumor activity and its 5'-triphosphate is a strong inhibitor of RNA and DNA syntheses in Ehrlich ascites tumor cells. Cordycepin gets incorporated as the terminal residue in RNA, while 3'-amino-3'-deoxy adenosine after getting incorporated becomes the 3'-terminal residue in tRNA (Suhadolnik 1970, 1979). The nucleoside antibiotic resulting from the

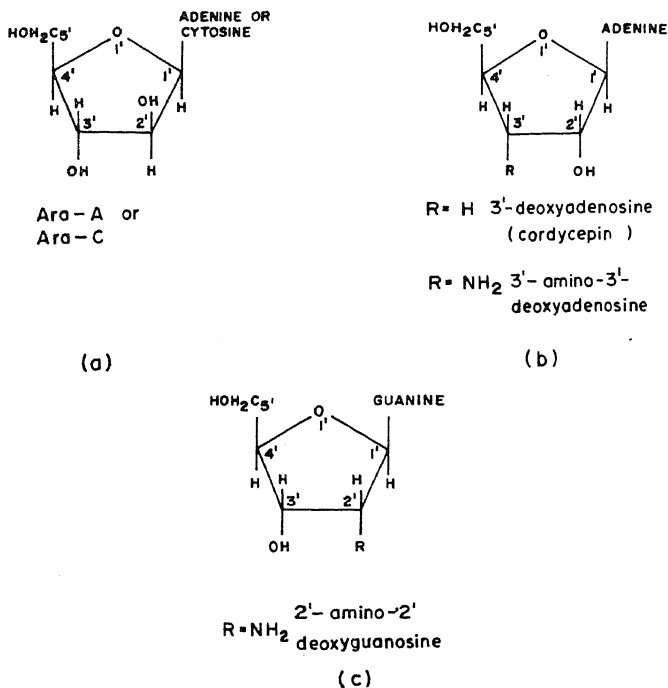


Figure 1. Nucleoside antibiotics resulting from sugar modifications.

replacement of the 2'-hydroxyl group by an amino group in guanosine is 2'-amino-2'-deoxy-guanosine (figure 1c). This antibiotic shows antitumor activity against HeLa cells and sarcoma 180 and also inhibits RNA and protein synthesis in *E. Coli* KY3591 (Nakanishi *et al* 1974, 1976, 1977).

Figure 2 shows some examples of modifications in the base part of the purine nucleosides. Tubercidin (figure 2a) results from the replacement of N(7) in adenosine by a —CH group. Further, the replacement of the hydrogen atom attached to C(7) of tubercidin by a cyano group ($-\text{C}\equiv\text{N}$) or a carboxamide group ($-\text{CONH}_2$) gives, respectively, toyocamycin and sangivamycin (figure 2a). Tubercidin possesses strong antitumor activity (Acs *et al* 1964; Bloch *et al* 1967) and is a inhibitor of RNA and DNA viruses (Bloch 1975a, 1975b). Toyocamycin is a strong antimicrobial agent (Matsuoka 1960) having significant antitumor activity (Sareyoshi *et al* 1965). Sangivanmycin is a strong antileukemic agent (Cairns *et al* 1967). All of them get phosphorylated to their 5'-triphosphates and then incorporated into RNA (Suhadolnik *et al* 1968a, b; Suhadolnik 1970). They also replace adenosine at the 3'-termini of tRNAs (Uretsky *et al* 1968). Formycin (figure 2b) has a 'C-C' sugar base linkage instead of the usual 'C-N' linkage. This antibiotic very efficiently substitutes for adenosine in many enzymatic reactions and also gets incorporated as the 3'-terminal residue of tRNA by replacing adenosine (Ward *et al* 1968, 1969a, b). The replacement of the amino group at C(6) in formycin by an oxygen atom results in formycin B. Both formycin and formycin B inhibit the influenza A₁ virus (Suhadolnik 1970). The above mentioned antibiotics are only a few examples of base modification in purine nucleosides. There are,

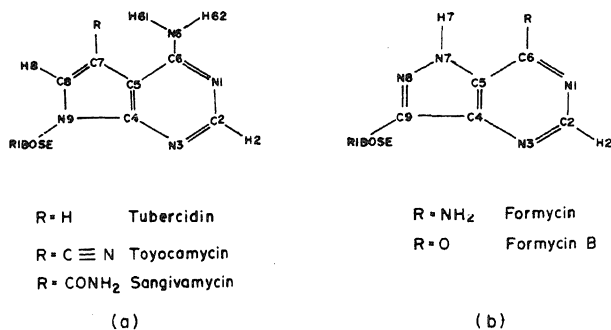


Figure 2. Nucleoside antibiotics resulting from purine base modifications.

however, a number of other examples which are well characterized and documented (Suhadolnik 1979).

Some examples of modifications in the base part of pyrimidine nucleosides are shown in figure 3. The replacement of C(6) in uridine and cytidine by a nitrogen atom results in 6-aza uridine (6-azaU) and 6-aza cytidine (6-azaC) (figures 3a, b), respectively, while in 3-deazauridine (3-deazaU) and 3-deazacytidine (3-deazaC) (figures 3c, d) it is the atom N(3) of the pyrimidine nucleosides which has been substituted by a carbon atom. 6-azaU and 6-azaC are both cancerostatic agents (Skoda 1963), whereas 3-deazaU and 3-deazaC exhibit cytostatic properties and inhibit the growth of several RNA viruses (Robins *et al* 1969). 5-substituted uridines and deoxyuridines (figure 4) have attracted considerable attention because of their antiviral and antitumor activity (Heidelberger 1965; Torrence *et al* 1978). 5-vinyl-2'-deoxyuridine (figure 4a) is not only an antiviral agent (Cheng *et al* 1976) but can also replace the parent nucleoside: thymidine in DNA of some organisms (Jones and Walker 1975). 5-ethynyl-2'-deoxyuridine (figure 4a) exerts strong activity against herpes simplex and vaccinia virus in culture and leukemia L1210 cells in culture (Sharma *et al* 1976). 5-amino uridine (figure 4b) is reported to have a wide range of biological activity inhibiting the growth of tumors and viruses (Gale *et al* 1972; Egert *et al* 1978). 5-aza cytidine which has C(5) atom of cytidine replaced by a nitrogen is a very potent antileukemic agent. It is readily incorporated into RNA and DNA and inhibits protein synthesis in bacterial, viral and mammalian cells (Sorm and Veseley 1964; Evans and Hanka 1968; Daskocil *et al* 1967). The above mentioned examples are only some of nucleoside antibiotics, the complete list of these antibiotics is available in the literature (Suhadolnik 1970, 1979).

We have been interested in the study of the conformations of some of these nucleoside antibiotics by using the PCILO method (Saran *et al* 1977; Mitra and Saran 1978; Saran and Mitra 1979; Saran and Chatterjee 1980a, b; Saran and Patnaik 1981, 1982, 1986; Patnaik and Saran 1984). The aim of these studies has been to understand why minor modifications or substitutions in pyrimidine and purine nucleosides leads to antibiotic activity of the modified nucleosides. In this review we would like to present the significant results which we have obtained on tubercidin (Saran and Mitra 1979), toyocamycin and sangivamycin (Saran and Chatterjee 1980a), cordycepin and 3'-amino-3'-deoxyadenosine (Saran and Patnaik 1981), 2'-amino-2'-deoxyadenosine (Patnaik and Saran 1984), 6-azauridine and 6-azacytidine (Mitra and Saran 1978), 3-deazauridine and 3-deazacytidine

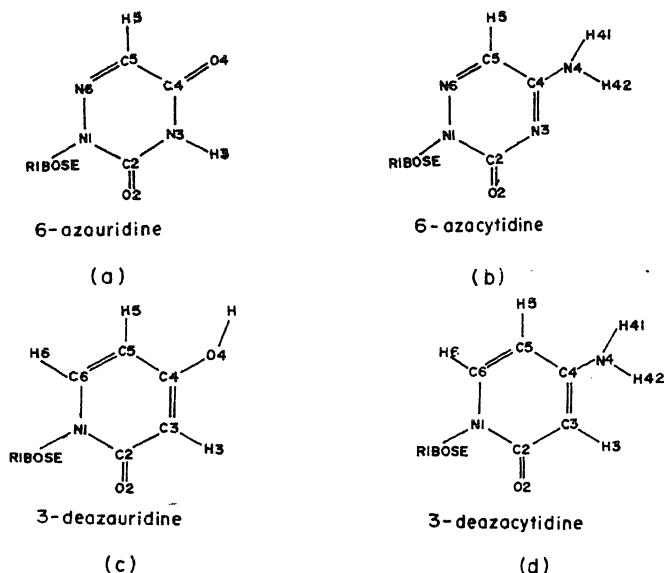


Figure 3. Nucleoside antibiotics resulting from pyrimidine base modifications.

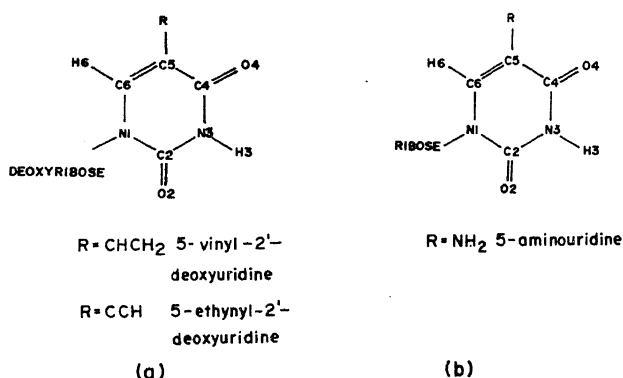


Figure 4. Nucleoside antibiotics resulting from pyrimidine base modifications.

(Saran and Chatterjee 1980b), 5-vinyl- and 5-ethynyl-2'-deoxyuridines (Saran and Patnaik 1982) and 5-aminouridine (Saran and Patnaik 1986). Besides these, arabinosyl nucleosides (Saran *et al* 1974) and formycins and showdomycin (Saran *et al* 1977) have also been investigated. However, these investigations are not as detailed as the other ones mentioned above.

2. Results and discussions

The method utilized in these investigations is the PCILO method (Pullman and Saran 1976; Jordan *et al* 1971). The torsion angles χ_{CN} (Sundaralingam 1960) and $\Phi_{\text{C4}'-\text{C5}'}$, $\Phi_{\text{C5}'-\text{O5}'}$, $\Phi_{\text{C3}'-\text{O3}'}$, and $\Phi_{\text{C2}'-\text{O2}'}$, (Saran *et al* 1972) as indicated in figure 5

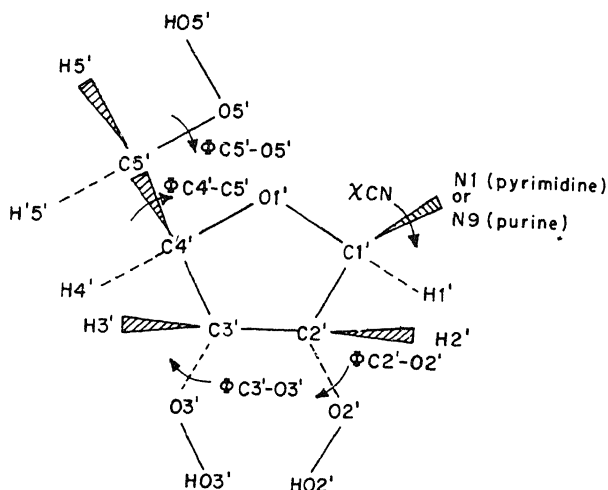


Figure 5. Torsion angles involved in nucleosides or nucleoside antibiotics.

determine the conformation of purine and pyrimidine nucleosides. These torsion angles are defined as:

$$\chi_{CN} = O(1')-C(1')-N(9)-C(8) \text{ or } O(1')-C(1')-N(1)-C(6)$$

$$\Phi_{C4'-C5'} = C(3')-C(4')-C(5')-O(5')$$

$$\Phi_{C5'-O5'} = C(4')-C(5')-O(5')-H(O5')$$

$$\Phi_{C3'-O3'} = C(2')-C(3')-O(3')-H(O3') \text{ and}$$

$$\Phi_{C2'-O2'} = C(1')-C(2')-O(2')-H(O2')$$

with the *cis*-planar arrangement of the terminal bonds being taken as zero for the torsion angle. The values of $\chi_{CN} = 0^\circ \pm 90^\circ$ and $180^\circ \pm 90^\circ$ correspond, respectively, to *anti* and *syn* regions (Sundaralingam 1960) while the values of $\Phi_{C4'-C5'} \approx 60^\circ, 180^\circ$ and 300° correspond to *gauche-gauche* (*gg*), *gauche-trans* (*gt*) and *trans-gauche* (*tg*) conformations around the exocyclic $C(4')-C(5')$ bond (Saran *et al* 1972; Pullman and Saran 1976) respectively. Besides these, the sugar ring puckering can be either $C(2')$ -endo or $C(3')$ -endo.

There are different possibilities of intramolecular hydrogen bonding between the sugar and the base and these are:

- (i) $O(5')-H(O5') \cdots N(3)$ of purine or
 $O(2)$ of pyrimidine base,

with the conditions: $\Phi_{C5'-O5'} = 60^\circ$ and $\Phi_{C4'-C5'} = 60^\circ$ (*gg*),
 and

- (ii) $O(2')-H(O2') \cdots N(3)$ or
 $O(2)$

with the condition: $\Phi_{C2'-O2'} = 60^\circ$

For the C(2')-endo sugar pucker, both intramolecular hydrogen-bonding (i) and (ii) are possible while in the case of C(3')-endo sugar pucker the second intramolecular hydrogen-bonding is not possible because of the fact that the participating atoms are farther apart than in the C(2')-endo sugar pucker (Saran and Chatterjee 1980a, b; Saran 1981). When these intramolecular hydrogen-bonds are allowed, the theoretical computations predict the most preferred conformation of the molecule as the one in which there is an intramolecular hydrogen-bonding. However, such intramolecular hydrogen-bonding is very unlikely to be preserved in aqueous solution. This is due to the fact that in aqueous solution the two hydrogen-bonding sites of the nucleoside or nucleoside antibiotics would rather be involved in two intermolecular hydrogen-bonds with water molecules than in one intramolecular hydrogen-bond. The situation in which both H(O5') and H(O2') are oriented away from the base, precludes the possibility of any of the intramolecular hydrogen-bonds and thus mimics the situations prevailing in the aqueous medium. This is achieved in theoretical calculations by prefixing the value of $\Phi_{C5'-O5'}$ and $\Phi_{C2'-O2'}$ equal to 180° and the conformations then obtained represent those occurring in the aqueous solution. The excellent agreement between theoretical predictions and the experimental observations in aqueous solutions on 8-azaadenosine (Saran *et al* 1978), tubercidin (Saran and Mitra 1979), 6-azauridine and 6-azacytidine (Mitra and Saran 1978), cordycepin (Saran and Patnaik 1981) and propranolol (Kulkarni *et al* 1979) has provided strong support to the above hypothesis. Since most of the biochemical reactions occur in aqueous medium, the results of the theoretical computations carried out on nucleoside antibiotics with the above mentioned conditions have very important biological significance. The important results of our studies have been summarized in tables 1 and 2.

2.1 Nucleoside antibiotics derived from purine nucleosides

The results on nucleoside antibiotics derived from purine nucleosides in table 1 indicate that conformational preferences of these antibiotics are very similar to their respective parent nucleosides. Highly localized global minima have been observed in the cases where the possibility of intramolecular hydrogen-bonding exists. For example, the conformation of the molecule is *syn-gg* in the case of intramolecular hydrogen-bonding through O(5')-H(O5') whereas in the case of O(2')-H(O2') it is *anti-gg*. However, in the absence of these intramolecular hydrogen bonds, the conformational preferences are highly flexible showing *syn-gg* $\rightleftharpoons$ *anti-gg* equilibrium with low barrier ($\sim 2-3$ kcal/mole) between the *syn* and *anti* regions. Ara-A (Saran *et al* 1974) and formycins (Saran *et al* 1977) also show large conformational flexibility when no intramolecular hydrogen-bonding is allowed.

2.2 Nucleoside antibiotics derived from pyrimidine nucleosides

Table 2 lists the results on nucleoside antibiotics derived from the pyrimidine nucleoside as well as the parent nucleosides and here also the conformational preferences of nucleoside antibiotics are very similar to those of the parent nucleosides and this similarity is specially profound in the case where no intramolecular hydrogen-bonding is allowed. Both *anti-gg* and *syn-gg* regions are

Table 2. Preferred conformations of nucleoside antibiotics derived from pyrimidine nucleosides.

Sugar pucker	Intramolecular hydrogen bonding with	6-azauridine* (Mitra and Saran 1978)	Uridine (Pullman and Berthod 1973; Pullman 1971)	6-azacytidine* (Mitra and Saran 1978)	Cytidine (Pullman and Berthod 1973; Pullman 1971)
		3-deazauridine (Saran and Chatterjee 1980b)	Berthod and Pullman 1971)	3-deazacytidine (Saran and Chatterjee 1980b)	Berthod and Pullman 1971)
C(2')-endo	O(5')-H(O5')	<i>syn-gg</i>	<i>syn-gg</i>	<i>syn-gg</i>	<i>syn-gg</i>
	O(2')-H(O2')	<i>anti-gg</i>	<i>anti-gg</i>	<i>anti-gg</i>	<i>anti-gg</i>
	None	<i>anti-gg,</i> <i>syn-gg</i>	<i>anti-gg,</i> <i>syn-gg</i>	<i>anti-gg,</i> <i>syn-gg</i>	<i>anti-gg,</i> <i>syn-gg</i>
	O(5')-H(O5')	<i>syn-gg</i>	<i>anti-gg</i>	<i>syn-gg</i>	<i>syn-gg</i>
C(3')-endo	None	<i>anti-gg,</i> <i>syn-gg</i>	<i>anti-gg,</i> <i>syn-gg</i>	<i>anti-gg,</i> <i>syn-gg</i>	<i>anti-gg,</i> <i>syn-gg</i>

* 6-azauridine and 6-azacytidine have not been investigated in as much detail as 3-deazauridine and 3-deazacytidine for the case in which no intramolecular hydrogen-bonding is allowed, but very similar results to those of 3-deazauridine and 3-deazacytidine are expected.

favourable with a slightly higher energy barrier (~ 3 to 5 kcal/mole) in between the *syn* and *anti* regions as compared to the antibiotics derived from purine nucleosides. The results on 5-vinyl- and 2'-ethynyl-2'-deoxyuridines show remarkably similar conformational preferences to those of the parent nucleoside: thymidine (Saran and Patnaik 1982). This is also true for 5-aminouridine (Saran and Patnaik 1986).

3. Biological significance

The results presented above clearly indicate that the nucleoside antibiotics have very similar conformational preferences to those of the parent nucleoside. This similarity is remarkably profound in the case where no intramolecular hydrogen-bonding is allowed as in aqueous solution. Since all biochemical reactions occur in aqueous media, the important implication of the above mentioned result is that these nucleoside antibiotics can very easily mimic the parent nucleosides and get incorporated in growing chains of RNA or DNA. This deduction is in agreement with experimental observations. Tubercidin, toyocamycin and sangivamycin get incorporated in tRNA by replacing the 3'-terminal adenosine residue and after incorporation they do not allow the normal functioning of the tRNA in terms of esterification of amino acids (Suhadolnik *et al* 1968a, b; Uretsky *et al* 1968). The activity of cordycepin and 3'-amino-3'-deoxyadenosine results from the fact that after incorporation into RNA, which has been experimentally observed (Suhadolnik 1970, 1979), they become terminal residues of RNA and the RNA synthesis stops. 2'-amino-2'-deoxyguanosine also gets incorporated in growing chains of RNA producing defective RNA which in turn inhibit protein synthesis. The experimental observations of Gassen *et al* (1972) indicate that 3-deazauridine gets substituted in the UUU codon of mRNA which specially interacts with phenylala-

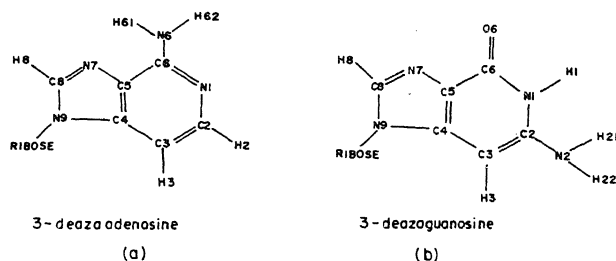


Figure 6. 3-deaza purine nucleosides.

nine of tRNA from yeast. The experimental observations on 5-vinyl-2'-deoxyuridine (Jones and Walker 1975) and 5-aminouridine (Egert *et al* 1978) are all in agreement with the deduction arrived at from theoretical studies (Saran and Patnaik 1982, 1986).

4. Conclusion

In conclusion it can be said that nucleoside antibiotics have very similar conformational preferences to those of the parent nucleoside from which they are derived. This similarity is highly profound in the situations that prevail in aqueous solution with the result that these antibiotics get incorporated in RNA and DNA by mimicking their parent nucleosides and then bring about the inhibition of RNA, DNA or protein synthesis. On the basis of these results, it has been possible to correlate the biological activity of these nucleoside antibiotics to the striking similarity of their conformational preferences to those of their parent nucleosides in the situations that prevail in aqueous solutions. Our theoretical studies on 3-deazaadenosine and 3-deazaguanosine shown in figure 6, indicate that these nucleoside analogs have very different conformational preferences as compared to their parent nucleoside (Saran and Chatterjee 1984). These two analogs have been experimentally shown to be biologically inactive (Cook *et al* 1975; Ikehara and Fukui 1974). The results on 3-deazaadenosine and 3-deazaguanosine clearly demonstrate that the converse of the correlation stated above for the biological activity of nucleoside antibiotics also holds true.

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Trends in the equilibrium theory of polyatomic fluids

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Abstract. The thermodynamics of polyatomic fluids is determined by the interactions between the polyatomic particles subject to the constraints imposed by the bonding within the polyatomic structure. One aspect of this work is the determination of the intermolecular potential function and the other is the calculation of multipoint correlation functions based on these potential functions. Trends in the calculation of these multipoint correlation functions are discussed and a semiempirical method of obtaining effective interactions is applied to the thermodynamics of fatty acid mixtures at the air/water interface.

Keywords. Correlation functions; interaction sites; effective diameters.

1. Introduction

The equilibrium structure of liquids is most conveniently described in terms of interparticle correlation functions (Percus 1964; Friedman 1985). In monatomic liquids, the atom-atom pair distribution function $g(r_{12})$ [or $g(12)$ or $g(r)$ or simply g] plays a central role and most thermodynamic quantities can be expressed as functionals of $g(r)$. Here $r_{12} = r = 12$ is the separation between particles 1 and 2. If one particle is held at the origin of a reference coordinate frame, the value of $g(r)$ at a distance r from the origin is the ratio of the local density at r and the bulk system density. The fluctuations in density appear as damped oscillations in $g(r)$. At large values of r , the influence of the particle at the origin diminishes and $g(r)$ approaches unity. The total correlation function $h(r) = g(r) - 1$ is related to the direct correlation function $c(r)$ through the Ornstein-Zernicke relation (1) which may be iterated as shown in (2)

$$h(12) = c(12) + \rho \int c(13)h(32) d3 = c(12) + \rho c * h, \quad (1)$$

$$= c(12) + \rho \int c(13)c(32) d3 + \rho^2 \int c(13)c(34)c(42) d3 d4 + \dots \quad (2)$$

The number density of particles is given by ρ , the integration variable is the coordinate of particle 3 and the convolution integral in (1) over the connecting coordinate is denoted by $*$.

By a graphical analysis $c(12)$ can be shown to be a sum of diagrams of the type shown in (3),

$$c(12) = \text{graph 1} + \text{graph 2} + \text{graph 3} + \text{graph 4} + \dots \quad (3)$$

Here, the white or unshaded circles represent coordinates 1 and 2 which are held fixed and a black circle represents multiplication by ρ and integration with respect to a position variable. A line connecting the circles is the Mayer f bond defined as $f(12) = \exp[-u(12)/k_B T] - 1$, where $u(12)$ is the pair potential between particles 1 and 2; k_B , the Boltzmann constant; and T , the system temperature. The sum in (3) is over all graphs which are at least doubly connected (except for the first one) i.e. wherein there are at least two independent paths connecting any pair of circles. The function $f(12)$ decays to zero at large r as $u(12)$ goes to zero. Since $c(12)$ is a collection of highly connected graphs, $c(12)$, is a more short ranged function (for non-ionic systems) than $h(12)$ and so it is a good function to be approximated by, e.g. the first few terms of (3). Some common approximations are the Percus-Yevick (PY), (4), and the hypernetted chain (HNC), (5), approximations for c .

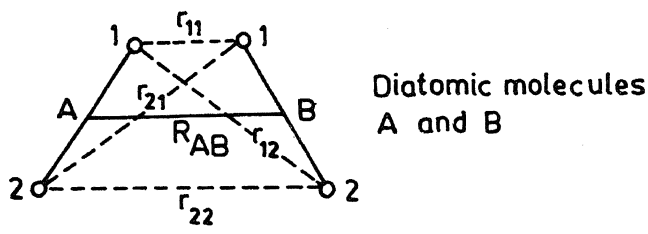
$$c = [\exp(-\beta u) - 1](1 + h - c), \quad (\text{PY}), \quad (4)$$

$$c = \exp(-\beta u - h - c) - h + c - 1. \quad (\text{HNC}), \quad (5)$$

Integral equations such as the ones shown above, along with perturbation theories, molecular dynamics and Monte Carlo computer simulations, form the main apparatus for the evaluation of the distribution functions and thermodynamic quantities for atomic fluids (Hansen and McDonald 1976).

In the study of molecular liquids, we need to specify the centre of mass R as well as the orientational coordinates Ω for each molecule. The pair distribution function between molecules A and B is now a functional of the potential $u(R_{AB}, \Omega_A, \Omega_B)$ where R_{AB} is the separation between the centres of mass of molecules A and B. These potentials are difficult to determine empirically or by quantum chemical calculations and it is customary to write the total pair potential as a sum of site-site interaction potentials (Chandler 1982).

$$u_{AB}(R_{AB}, \Omega_A, \Omega_B) = \sum_{\alpha A, \beta B} u_{\alpha A, \beta B}(r_{\alpha\beta}). \quad (6)$$



Here $r_{\alpha\beta}$ is the distance between site α on molecule A and site β on molecule B. These sites are normally taken as the atomic centres on molecules A and B. One of the typical forms for the site-site potential is the 12-6-1 potential defined by

$$u_{\alpha A, \beta B}(r_{\alpha\beta}) = C_{\alpha A, \beta B} r_{\alpha\beta}^{-12} - D_{\alpha A, \beta B} r_{\alpha\beta}^{-6} + q_{\alpha A} q_{\beta B} r_{\alpha\beta}^{-1}, \quad (7)$$

where C and D are the coefficients similar to the Lennard-Jones potential and $q_{\alpha A}$ and $q_{\beta B}$ are the charges on the sites α and β on molecules A and B .

The integral equation (1) for the site-site total correlation function is written as (Chandler and Anderson 1972)

$$h_{\alpha A, \beta B} = \sum_{\substack{\delta, \lambda \\ (\text{sites})}} \omega_{\alpha A, \delta A} * c_{\delta A, \lambda B} * \omega_{\lambda B, \beta B} \\ + \sum_S \sum_{\substack{\delta, \lambda \\ (\text{sites})}} \omega_{\alpha A, \delta A} * c_{\delta A, \lambda S} * \rho_S h_{\lambda S, \beta B}. \quad (8)$$

The total intramolecular equilibrium site-site pair correlation function is denoted by ω , ρ_S denotes the density of each species S in a multicomponent liquid and $*$ denotes the convolution integral over intermediate coordinates as in (1). The quantity ω is defined in terms of $S_{\alpha\gamma}(r)$, the equilibrium pair correlation function between distinct sites in the liquid state

$$\omega_{\alpha A, \gamma B}(r) = \delta_{\alpha\gamma} \delta(r) + (1 - \delta_{\alpha\gamma}) S_{\alpha\gamma}(r). \quad (9)$$

Here, $\delta_{\alpha\gamma}$ is the Kronecker δ and $\delta(r)$ is the Dirac delta function.

In addition to the Ornstein-Zernicke equation (8), one needs closure relations like (4) and (5) to solve for the site-site pair correlation functions. The integral equation for the interaction site models (ISM) has been solved for nonionic systems such as N_2 and CCl_4 with the PY closure (Chandler 1978) and for polar and ionic systems like HCl , Br_2 and ions in water using the HNC closure (Rossky 1985). Another approach to molecular liquids is via computer simulations, wherein care has to be taken so that the intramolecular distances have to remain constant within some tolerance during the simulation (Rychaert 1977).

In the next section a semiempirical method to describe the thermodynamics of monolayers at the air/water interface is outlined. When the interacting molecules in the molecular liquid are complex (Wiegel and Cox 1980), the methods outlined above are not very easy to apply and this necessitates the search for methods which can be readily used by the experimentalist.

2. Method and Results

In complex molecular fluids a convenient approximation is to look for orientationally averaged intermolecular potentials and then use the formalism of atomic fluids to calculate the thermodynamic quantities. The orientationally averaged or median $u_0(r)$ potential may be evaluated from

$$\int d\Omega \text{sign}[u(r, \Omega) - u_0(r)] = 0. \quad (10)$$

Here Ω denotes relative orientational coordinates between molecules A and B , the sign function takes the sign of the argument and $u(r, \Omega)$ is the true anisotropic potential. Such a procedure has worked well for simple systems like the diatomic fluid N_2 (Johnson *et al* 1984).

This procedure becomes quite tedious and has not been tested for molecules with a large number of internal degrees of freedom. In systems of dimensionality less than three, like monolayers or a one-dimensional system, the extent of averaging is considerably reduced. Now we shall analyse the role of intermolecular interactions on the thermodynamics of fatty acid monolayers at the air/water interface.

Experimental surface pressure area isotherms for a few fatty acids (curves A to D) are shown in figure 1. The isotherm calculated for a simple fluid such as a hard disk system of diameter $3.5 \text{ \AA}$ by any of the methods outlined in the introduction (in this case from the solutions of the Yvon-Born-Green equation) is also shown in the figure for comparison (curve E). The thermodynamics of even the soft core atomic systems where the interatomic potentials are continuous (such as a Lennard-Jones potential) is known to be very similar to that of curve E. The dissimilarity between the two-dimensional hard core model and the displayed experimental data is simply an indication of the dominant influence of the orientational dependence of the potential. In the semiempirical method presented here we use corresponding states or scaling ideas and define an effective size parameter σ_{eff} at a given surface pressure as:

$$\rho \sigma_{\text{eff}} = \rho_R \sigma_R^2. \quad (11)$$

Here ρ_R and σ_R are the densities and diameters of the reference hard disk fluid and ρ is the density of the actual system. The effective diameters σ_{eff} for some acids as a function of density obtained from (11) are shown in figure 2 (curves A to C). This parameter is a representation of the orientational forces between the molecules. When the system density increases, the molecules on the average come closer and an increase in the extent of nonbonding interactions is represented by an increased effective diameter. It is also found that the effective diameters of bent molecular

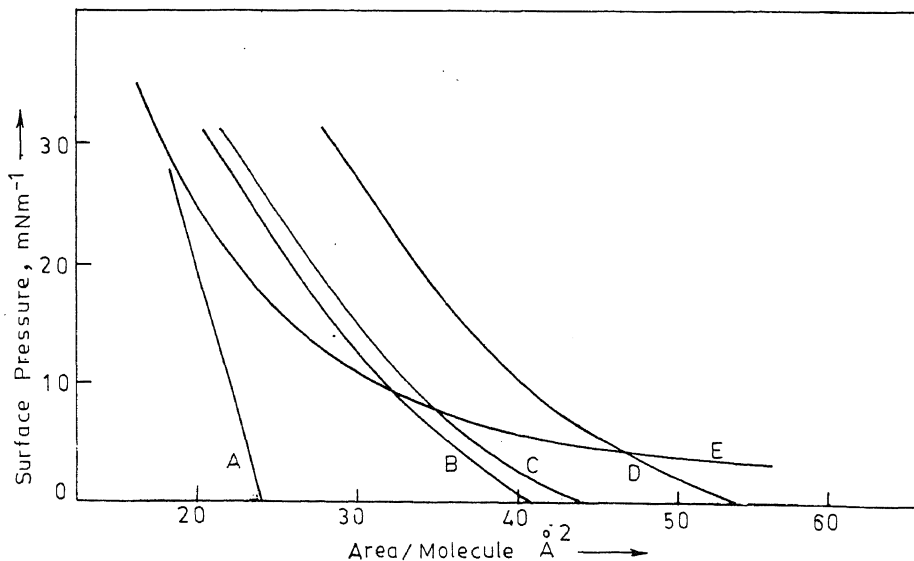


Figure 1. Pressure area isotherms for arachidic acid (curve A), oleic acid (D), 2:3 mixture of oleic and arachidic acids (B), and 52:48 mixture of oleic and arachidic acids (C). Curve E is the pressure area isotherm for hard disks with $\sigma = 3.5 \text{ \AA}$.

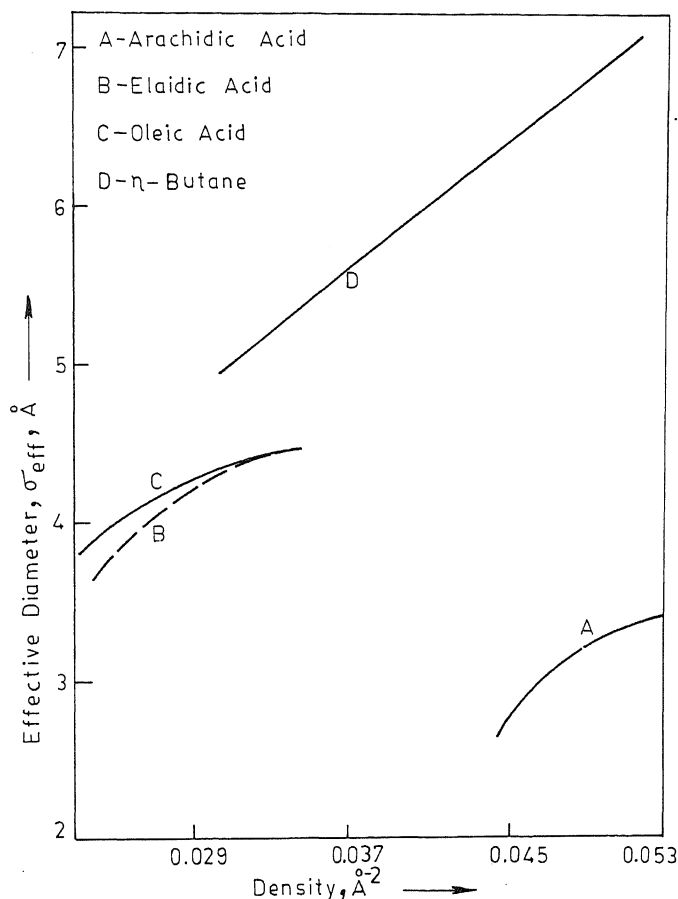


Figure 2. Effective diameter as a function of density for arachidic acid (curve A), elaidic acid (B) and oleic acid (C) and the calculated effective diameters for *n*-butane (curve D).

chains such as oleic acid (*cis*) are greater than the effective diameters of straight chains of elaidic acid (*trans*) due to an increased contact between bent chains (Nagalakshmi 1985; Nagalakshmi and Tembe 1987).

A practical utility of these effective diameters is in the calculation of the surface pressures of the mixtures from the effective diameters of the components σ_1 and σ_2 (Venkateshwara Rao 1986; Venkateshwara Rao and Tembe 1987). At a given density, the effective diameter of the binary mixture σ_{mix} is obtained from those of its components by the equation

$$\sigma_{\text{mix}}^2 = X_1 \sigma_1^2 + (1 - X_1) \sigma_2^2, \quad (12)$$

where X_1 is the mole fraction of component 1. Knowing σ_{mix} we can get ρ_R from (11) and thereby the pressure of the system. The pressures calculated from (12) are in fair agreement with experiment (Feher *et al* 1977; Venkateshwara Rao 1986).

The next task is the evaluation of the effective areas from site-site pair potentials. For this, we take two *n*-butane molecules A and B which are placed on a planar surface. Molecule A is fixed. At a given distance r between the two chains, the

effective pair potential is obtained by averaging over the orientations of the molecule B. In the present calculation, site-site Lennard-Jones potentials with $\sigma = 2.4 \text{ \AA}$ and $\epsilon = 50 \text{ K}$ are used for all pairs of atoms. For each value of r , 72 conformations on molecule B were considered for obtaining the effective potential. The effective potential rises faster than the site-site potential in the repulsive region and decays to zero more rapidly in the attractive region. The repulsive parts of the effective and the site-site potentials are shown in figure 3. At each value of r a Lennard-Jones potential with a different value of σ is seen to have the same value as the effective potential. Taking r to be a measure of the average distance of molecular separation, the density may be obtained as $\rho \sim 1/r^2$. A plot of σ as a function of density for *n*-butane obtained from the data of figure 3 is shown in figure 2 (curve D). These effective diameters show the same qualitative trend as the experiment although the systems compared are of different chainlengths.

While there is need to optimise the number of configurations in the averaging procedure and even to use Boltzmann weighted averages, the semiempirical

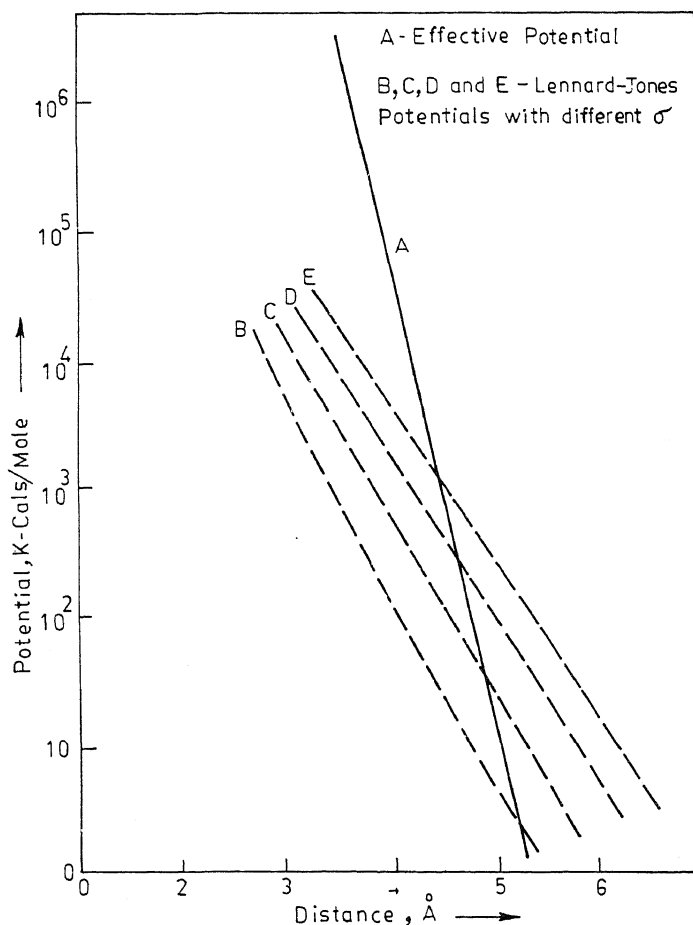


Figure 3. Rotationally averaged effective potential for *n*-butane (curve A) and Lennard-Jones potentials with different values of σ . The σ values for the curves are B (5.35 Å), C (6.0 Å), D (6.5 Å) and E (7 Å).

approach outlined here is useful for correlating the experimental data with effective size parameters which can be readily evaluated. The effective size as a function of the number of carbon atoms in the chains is being investigated. When the thermodynamics of the mixture does not match the thermodynamics obtained from σ_{mix} , additional parametrizations of molecular size with an effective diameter and an effective length may be needed. There is also need to systematically reduce the number of degrees of freedom in complex molecules so that the integral equations for interaction site models can be efficiently solved.

Acknowledgements

I would like to thank M Nagalakshmi and S Venkateswara Rao for their help in computations of effective areas.

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Synthesis and spectroscopic investigations of complexes of lanthanide nitrates with 5-nitroisoquinoline-2-oxide

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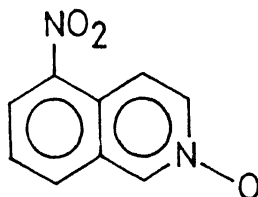
MS received 9 January 1987

Abstract. New complexes of lanthanide nitrates with 5-nitroisoquinoline-2-oxide (NI-QNO) of the type $\text{Ln}(\text{NIQNO})_3(\text{NO}_3)_3$ where $\text{Ln} = \text{La}-\text{Yb}$ and Y have been synthesised and characterised by analyses, conductance, infrared, proton NMR and electronic spectra. The molar conductance and IR data point to the coordinated nature of the nitrate groups in all the complexes studied. IR spectral analysis along with the proton NMR spectra of the ligand and its (diamagnetic) La^{3+} and Y^{3+} complexes unequivocally proves that the coordination of the ligand to the tripositive lanthanide ions taken place through the oxygen of the N-O group. From a comparison of the visible electronic spectral shapes of the Nd^{3+} and Ho^{3+} complexes, a probable coordination number of eight can be assigned to all the complexes.

Keywords. Lanthanide nitrate complexes; 5-nitroisoquinoline-2-oxide; infrared; proton NMR; electronic spectra.

1. Introduction

Investigations on the lanthanide complexes of substituted pyridine-1-oxides with substituents other than the methyl group, have led to the conclusion that substituents at the 4-position of the heterocyclic ring are capable of introducing a steric hindrance to coordination and consequently affect the ligand to metal ratio as compared to that in the substituted pyridine-1-oxide complexes (Navaneetham and Soundararajan 1981). To understand the effect of the substituents on the coordination number around the metal ion due to the differences in their nature such as their position in the ring, the bulkiness, electron-donating or -withdrawing tendency, new complexes of lanthanide nitrates with 5-nitroisoquinoline-2-oxide have been synthesised and studied by analyses, conductance, IR, proton NMR and electronic spectra.



2. Experimental

2.1 Materials

Isoquinoline was obtained from Fluka Chemicals, Germany. Lanthanide oxides (99.99% pure) were obtained from the American Potash and Chemicals, USA. All the solvents were purified by standard methods.

5-nitroisoquinoline was prepared by nitration of isoquinoline-2-oxide as described by (Katritzky *et al* 1957) for 4-nitropyridine-1-oxide and recrystallized from chloroform solution (m.p. 219–220°C; Lit., Ochiai and Ishikawa 1945, 220–222°C). Hydrated lanthanide nitrates were prepared as reported earlier (Rajasekar and Soundararajan 1979).

2.2 Preparation of the complexes

A solution of lanthanide nitrate (1 mmole) in hot ethyl acetate (15 ml) was added slowly with stirring to a boiling solution NIQNO (15 mmoles) in ethyl acetate (200 ml). The stirring was continued for 5 minutes. The precipitated complex was filtered through a sintered crucible (G_3), washed with hot chloroform followed by diethyl ether and finally dried over phosphorus(V) oxide in a vacuum desiccator.

2.3 Analytical and physical methods

The metal and anion content of the complexes were estimated by EDTA titrations using xylenol-orange as indicator (Lyle and Rahman 1963). The anion was estimated by gravimetric precipitation with nitron as described by (Welcher 1947). The ligand was estimated spectrophotometrically at 204 nm using the calibration curve method (Willard *et al* 1965). The analytical data are presented in table 1. The IR spectra of the ligand and its lanthanide complexes in nujol (in the region 400–4000 cm^{-1}) were recorded on a Perkin-Elmer model 397 spectrophotometer. The important IR bands and their assignments are given in table 2. Proton NMR spectra of the ligand and its diamagnetic La^{3+} and Y^{3+} complexes were recorded on a Bruker WH-270 spectrometer operating in the FT mode, using CD_3CN as solvent and TMS as the internal reference (table 3). Electronic spectra of Nd^{3+} and Ho^{3+} complexes in acetonitrile were recorded in the visible region on a Hitachi uv-3400 model spectrophotometer. The solid state spectra for the same complexes

Table 1. Analytical and conductivity data for the complexes of the general formula $\text{Ln}(\text{NIQNO})_3(\text{NO}_3)_3$.

Ln^{3+}	% Metal		% Ligand		% Anion		* Molar conductance in CH_3CN
	Found	Calc.	Found	Calc.	Found	Calc.	
La	15.48	15.52	63.84	63.69	20.70	20.78	14
Nd	16.14	16.02	63.53	63.32	20.84	20.66	13
Ho	17.84	17.91	61.64	61.89	20.40	20.20	24
Er	18.19	18.12	61.90	61.74	20.04	20.15	17
Yb	18.56	18.63	61.41	61.35	20.22	20.02	18
Y	9.28	9.41	—	—	—	—	20

* Values in $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, at 25°C

Table 2. Important infrared frequencies (in cm^{-1}) and their assignments for NIQNO and its nitrate complexes.

NIQNO	La	Nd	Ho	Er	Yb	Y	Assignment
—	1790vw	1785vw	1790w	1785w	1785w	1785w	$(\nu_2 + \nu_3)$
—	1760vw	1760vw	1765vs	1765vs	1765vs	1768s	nitrate
—	1728w	1728vw	1728vs	1728vs	1730vs	1730s	$(\nu_2 + \nu_5)$ nitrate
1522vs	1528vs	1528vs	1528vs	1525vs	1522vs	1525s	ν_4 nitrate + ligand
1340s	1332vs	1335vs	1338v	1335vs	1335s	1330vs	ν_{NO} deformation
—	1310s	1305s	1325s	1305s	1305vs	1295s	ν_1 nitrate
—	1030vs	1030vs	1030vs	1025vs	1028vs	1028s	ν_2 nitrate
840m	845w	850vw	845m	845m	845m	845m	δ_{NO}
739m	740m	742m	745vs	742vs	745vs	745vs	γ_{CH}

Table 3. Proton NMR data for NIQNO and its La^{3+} and Y^{3+} complexes in CD_3CN .

Compound	Chemical shifts with respect to TMS (δ)					
	1H	3H	4H	6H	7H	8H
NIQNO	8.84	8.48	7.94	8.38	7.71	8.17
La^{3+}	9.68	8.54	8.11	8.42	7.84	8.26
Y^{3+}	9.68	8.65	8.15	8.56	7.89	8.34

in nujol were recorded in the same region were run on a Cary-14 instrument. Electrolytic conductance measurements in acetonitrile solutions of the complexes were carried out with a Siemens conductivity bridge using an immersion cell (type LTA), previously calibrated with standard KCl solution. The concentration of the solutions used were of the order of 10^{-3} M.

3. Results and discussion

Analytical data for the newly prepared complexes listed in table 1 indicate that three molecules of the ligand are associated with each metal ion. All the complexes are soluble in DMSO, DMF and acetonitrile (Ho^{3+} , Er^{3+} and Yb^{3+} complexes are slightly insoluble) and insoluble in chloroform, benzene and carbon tetrachloride. Molar conductance values suggest that all the three nitrate groups are non-ionic in nature (Geary 1971).

The absence of the two IR active bands of the nitrate ion D_{3h} symmetry in all the complexes at 720 and 1390 cm^{-1} provides confirmatory evidence to the conductance measurements that all the nitrate groups are non-ionic in nature. Nitrate groups are capable of bonding to a metal ion in monodentate or bidentate fashion, in either case the symmetry is lowered from D_{3h} to C_{2v} . The two situations cannot, in general, be unambiguously distinguished on the basis of the IR data alone. The combination bands of the nitrate group which generally appear in the 1700–1800 region have been used for structural assignments of the nitrate groups (Curtis and Curtis 1965; Lever *et al* 1971). In the present complexes, the presence of three weak

bands in the said region and the separation between them suggest that both mono and bidentate nitrate groups are present in the complexes studied.

The band at 1340 cm^{-1} assigned to N–O stretching frequency of the ligand shifts to lower frequencies (ca. $5\text{--}8\text{ cm}^{-1}$) in the spectra of the complexes indicating the binding of the N-oxide oxygen to the tripositive lanthanide ion. The $\nu\text{N--O}$ and C–H out-of-plane vibrations at 840 cm^{-1} and 739 cm^{-1} of the ligand shift to higher frequencies revealing the coordination of the N–O group to the metal ion in the NIQNO complexes of lanthanide nitrates.

Additional evidence for the participation of the oxygen of the N–O moiety in coordination with the lanthanide ion is found in the proton NMR spectra of the ligand and its diamagnetic complexes (La^{3+} and Y^{3+}) (table 3). The assignments have been made relative to the reported assignments for 5-nitroisoquinoline (Aramarego and Batterharn 1966).

All proton signals in the La^{3+} and Y^{3+} complexes show downfield shifts, confirming the coordination of the N-oxide moiety to the lanthanide ion. The observed deshielding is a consequence of the drainage of electron density towards the lanthanide ion in the complexes. The downfield shifts observed in the Y^{3+} complexes are greater than those in La^{3+} complexes, showing the stronger coordination of the ligand through the oxygen of the N-oxide moiety to the metal ion. The variation in the magnitude of deshielding of the heterocyclic ring protons in the lanthanide nitrate complexes (La^{3+} and Y^{3+}) of NIQNO (in comparison with IQNO complexes, Rajasekar 1986), is a consequence of the influence of the substituents at the 5-position of the isoquinoline-2-oxide ring on the strength of the metal-ligand bond.

Electronic spectral data are given in table 4. The sharp $f\text{--}f$ bands exhibit red shifts with respect to the aquo ions consequent on complex formation. The red shift called the nephelauxetic shift, is a measure of the covalency in the metal-ligand bond. Sinha (1966, 1971) has proposed a δ scale to express the covalent character of the metal-ligand bond, which is given by the relation,

$$\delta(\%) = [(1 - \beta)/\beta] \times 100,$$

where β is the average value of the ratio $\nu\text{ complex}/\nu\text{ aquo}$. The δ values calculated for Nd^{3+} and Ho^{3+} complexes of NIQNO are presented in table 4. The shapes of the hypersensitive bands of the Nd^{3+} and Ho^{3+} complexes resemble

Table 4. Electronic spectral data and their assignments (in DMSO).

Nd^{3+}		Ho^{3+}	
<i>J</i> level	Energy (KK)	<i>J</i> level	Energy (KK)
$4G_{9/2}$	19.53	$5F_3$	20.52
$4G_{7/2}$	19.02	$5F_4, 5F_{5/2}$	18.47
$2G_{7/2}$	17.13	$5F_5$	15.35
$4G_{5/2}$			
$\delta = 0.9897$		$\delta = 1.07$	

markedly the shapes of the eight-coordinate lanthanide perchlorate complexes of N-(2-pyrimidyl)benzamide (Rajasekar 1980).

The position, shape and relative intensities were found to be identical both in the solid state spectra recorded in Nujol and in the solution spectra taken in acetonitrile. In short, the same eight-coordinate geometry is observed in both the states and, hence, the compatibility in the solid state properties, such as infrared and solution properties as well as conductivity and NMR.

On the basis of the available evidence, a tentative coordination number of eight can be suggested for all the complexes of NIQNO.

Acknowledgements

The author is thankful to CSIR, New Delhi, for a Pool Officer position, the authorities of the Indian Institute of Science, Bangalore, for facilities and the Sophisticated Instrument Facility for the NMR spectra.

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Inter-ligand stacking interactions in some *o*-phenanthroline amino acid biligand complexes

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MS received 19 January 1987; revised 24 April 1987

Abstract. Biligand complexes of the type metal/*o*-phenanthroline/amino acid, where metal = Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} ; and amino acid = β -phenyl alanine or tryptophan have been found to show inter-ligand stacking interactions in aqueous solutions. This interaction has been evaluated quantitatively from a knowledge of the formation constants of these complexes (and that of the identical biligand complex with α -alanine) as determined by potentiometric pH titrations at 25°C and an ionic strength, $I = 0.2$ (mol dm^{-3} , KNO_3) by following the Irving-Rossotti approach. The sequence of interaction is tryptophan > β -phenyl alanine.

Keywords. Stacking interactions; biligand metal-phenanthroline-amino acid complexes.

1. Introduction

Stacking interactions in biligand complexes are included in general category of hydrophobic interactions (Sigel and Fischer 1980). The hydrophobic effect is the most important single factor which governs the organization of the constituent molecules of living matter into complex structural entities (Tanford 1973). These inter-ligand interactions enhance the stability of the biligand complexes. Since *o*-phenanthroline is structurally similar to porphyrins, its simultaneous bonding with biochemically important metal ions and amino acids make a useful study. This has prompted us to design the present ternary systems of the type [MAL], where M = Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} or Cd^{2+} ; A = *o*-phenanthroline (*phen*); L = α -alanine (α -*ala*), β -phenyl alanine (β -*phe*) or tryptophan (*try*). An attempt has been made to demonstrate quantitatively the extent upto which extrastabilization is caused due to stacking.

2. Experimental

All chemicals used were of standard purity (BDH analar/Merck GR). The solutions were prepared in double distilled water. The strength of the metal solutions was adjusted finally after their complexometric titrations with EDTA (West 1969). The metal and ligand solutions of 1.0×10^{-3} mol dm^{-3} (final)

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concentration and an NaOH solution of 0.2 mol dm^{-3} concentration were used. The formation constants were determined by means of potentiometric pH-titrations in aqueous medium at 25°C and an ionic strength, $I = 0.2 \text{ (mol dm}^{-3}, \text{KNO}_3\text{)}$ by following the Irving-Rossotti approach (Irving and Rossotti 1953, 1954; Bhattacharya and Chidambaram 1970). An Elico digital pH-meter (model LI-120) was used for pH measurements. The titrations were repeated to obtain reproducible pH data. The proton-ligand formation constants ($\log K_n^H$) were redetermined in order to get their values under experimental conditions. These were used in the evaluation of metal-ligand formation constants ($\log K_{ML}^M$ and $\log K_{MAL}^{MA}$). The formation constants were refined by the method of linear plots (Rossotti and Rossotti 1955) and also subjected to statistical refinement by the 'Q-test' (Pecsok *et al* 1976).

3. Results and discussion

The calculated values of formation constants and $\Delta \log K$ ($= \log K_{MAL}^{MA} - \log K_{ML}^M$) are presented in table 1. Figures in parentheses represent standard deviations. It may be seen that the $\Delta \log K$ values with α -ala are uniformly negative with all the metal ions, but with β -phe these values are less negative or even positive (with Cu^{2+}), and with *try* all the values are positive. Less negative or positive values of $\Delta \log K$ indicate greater stabilization of the biligand complexes. This is significant as normally one would expect the β -phe and *try* biligand complexes to be less stable ($\Delta \log K$ more negative) because of their bulkier side chains ('phenyl' with β -phe and 'indole' with *try*). Greater stabilization

Table 1. Formation constants of the binary ML and ternary MAL complexes. Temperature = 25°C Ionic strength, $I = 0.2 \text{ (mol dm}^{-3}, \text{KNO}_3\text{)}$

Formation constant	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
<i>α-ala</i>					
$\log K_{ML}^M$	4.71	5.83	7.83	5.29	4.85
	(± 0.03)	(± 0.02)	(± 0.03)	(± 0.02)	(± 0.02)
$\log K_{MAL}^{MA}$	4.34	5.28	7.17	4.94	4.58
	(± 0.02)	(± 0.02)	(± 0.02)	(± 0.03)	(± 0.01)
$\Delta \log K$	-0.37	-0.55	-0.66	-0.35	-0.27
<i>β-phe</i>					
$\log K_{ML}^M$	3.89	4.83	7.34	4.57	4.21
	(± 0.03)	(± 0.03)	(± 0.02)	(± 0.03)	(± 0.01)
$\log K_{MAL}^{MA}$	3.60	4.54	7.60	4.35	4.04
	(± 0.01)	(± 0.01)	(± 0.03)	(± 0.02)	(± 0.03)
$\Delta \log K$	-0.29	-0.29	+0.26	-0.22	-0.17
<i>try</i>					
$\log K_{ML}^M$	4.10	5.50	8.08	4.79	4.33
	(± 0.03)	(± 0.03)	(± 0.03)	(± 0.02)	(± 0.02)
$\log K_{MAL}^{MA}$	4.50	5.75	8.69	5.11	4.59
	(± 0.02)	(± 0.01)	(± 0.02)	(± 0.02)	(± 0.03)
$\Delta \log K$	+0.40	+0.25	+0.61	+0.32	+0.26

Note: Values in parentheses are standard deviations.

of these complexes is a consequence of inter-ligand stacking interaction in the β -*phe* and *try* biligand complexes. The extrastabilization caused due to this may be worked out from a knowledge of the experimental values of $\log K_{\text{MAL}}^{\text{MA}}$ and $\Delta \log K$. The quantity $\Delta \log K$ may be regarded as an equilibrium constant for the reaction



Another stability quantifying parameter $\Delta \Delta \log K$ may be defined as

$$\Delta \Delta \log K = \Delta \log K_1 - \Delta \log K_s, \quad (2)$$

where $\Delta \log K_1$ and $\Delta \log K_s$ stand for the experimental values of $\Delta \log K$ with the 'large-sized' (β -*phe*, and *try* in the present case) and 'small-sized' (here α -*ala*) ligands, respectively. The calculated values of $\Delta \Delta \log K$ are reported in table 2; positive and significant values qualitatively indicate extrastabilization due to stacking interaction between the primary and secondary ligands within the ternary system. $\Delta \Delta \log K$ may also be regarded as equilibrium constant for the reaction



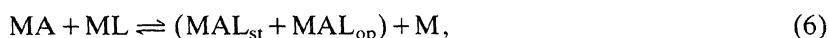
involving ligand selectivity. The subscripts 'l' and 's' mean the same as defined above. We may conceive of the existence of an equilibrium of the type



(where MAL_{op} = 'open' and MAL_{st} = 'stacked' forms of MAL) in view of the fact that the $\Delta \Delta \log K$ values are quite small as compared to $\log K_{\text{MAL}}^{\text{MA}}$ suggesting that rather weak forces are involved in stacking. The equilibrium constant, K_l , corresponding to this equilibrium will evidently be dimensionless and may be written as

$$K_l = [\text{MAL}_{\text{st}}]/[\text{MAL}_{\text{op}}], \quad (5)$$

Equation (1) can be written in two ways,



and



for the existence or absence of stacking interaction, respectively. These would in

Table 2. $\Delta \Delta \log K$ values, equilibrium constant (K_l), and percentage of stacked form (% MAL_{st}) in the ternary systems.

System	Property	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺
<i>M. phen.</i> (β - <i>phe</i> / α - <i>ala</i>)	$\Delta \Delta \log K$	+0.08	+0.26	+0.92	+0.13	+0.10
	K_l	0.20	0.81	7.31	0.34	0.25
	(%) MAL_{st}	24.00	44.00	87.96	25.00	31.25
<i>M. phen.</i> (<i>try</i> / α - <i>ala</i>)	$\Delta \Delta \log K$	+0.77	+0.80	+1.27	+0.67	+0.53
	K_l	4.88	5.30	17.62	3.67	2.38
	(%) MAL_{st}	82.99	84.12	94.62	78.58	70.40

turn lead to two modified values of $\Delta \log K$ (corresponding to (6) and (7), respectively) as

$$\Delta \log K_{\text{exp}} = [\text{MAL}_{\text{st}} + \text{MAL}_{\text{op}}] [\text{M}]/[\text{MA}] [\text{ML}], \quad (8)$$

(subscript 'exp' stands for 'experimental') and

$$\Delta \log K_{\text{op}} = [\text{MAL}_{\text{op}}] [\text{M}]/[\text{MA}] [\text{ML}]. \quad (9)$$

Assuming the $\Delta \log K_{\text{op}}$ value as equal to the experimental $\Delta \log K$ value for the 'small-sized' ligand, combination of (2), (5), (8) and (9) and rearrangement of terms gives K_I in terms of $\Delta \log K$ as

$$K_I = 10^{\Delta \log K} - 1. \quad (10)$$

The percentage of stacked form (% MAL_{st}) may be expressed as

$$(\%) \text{MAL}_{\text{st}} = [K_I/(1 + K_I)] \times 100. \quad (11)$$

The values of K_I and (%) MAL_{st} for the β -*phe* and *try* biligand complexes (in comparison to the α -*ala* biligand complex regarding the $-\text{CH}_3$ side-chain in α -*ala* as negligible for the present purpose) have been calculated using (10) and (11) above and shown in table 2. These values show greater stacking interaction with *try* than with β -*phe*. It seems that the larger indole moiety in *try* as compared to a smaller phenyl moiety in β -*phe* is responsible for the sequence *try* > β -*phe*. For the same reason perhaps the variations in K_I and (%) MAL_{st} values are larger with β -*phe* than with *try*.

The data on energetics of the formation of biligand complexes and their extrastabilization have been recorded in table 3. The free-energy changes ΔG_1 and ΔG_2 correspond to $\log K_{\text{MAL}}^{\text{MA}}$ and $\Delta \log K$ values, respectively. The extent of extrastabilization may be expressed as

$$(\%) \text{stabilization} = (\Delta G_2/\Delta G_1) \times 100. \quad (12)$$

The biligand complexes with *try* and β -*phe* are extrastabilized by about 0.10 to 1.73 kcal mole⁻¹. This range agrees well with the theoretical calculations on inter-ligand (intramolecular) interactions (Scheraga 1979). The (%) stabilization values lie in the range 2.2 to 17.1%; a similar observation has been reported (Sigel

Table 3. Energetics of complexation : ΔG_1 ($= -2.303 RT \cdot \log K_{\text{MAL}}^{\text{MA}}$) and ΔG_2 ($= -2.303 RT \cdot \Delta \log K$) values-(in kcal mole⁻¹) and (%) stabilization of the ternary complexes.

System	Property	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺
<i>M. phen.</i>	$-\Delta G_1$	4.90	6.18	10.35	5.92	5.50
(β - <i>phe</i> / α - <i>ala</i>)	$-\Delta G_2$	0.1090	0.3543	1.2539	0.1771	0.1363
<i>M. phen.</i> β - <i>phe</i>	(%) Stabilization	2.22	5.73	12.11	2.99	2.47
<i>M. phen.</i>	$-\Delta G_1$	6.13	7.83	11.84	6.96	6.25
(<i>try</i> / α - <i>ala</i>)	$-\Delta G_2$	1.0495	1.0904	1.7310	0.9132	0.7223
or						
<i>M. phen.</i> <i>try</i>	(%) Stabilization	17.10	13.92	14.61	13.12	11.55

and Fischer 1980) for the biligand *phen* complexes with aliphatic amino acids like leucine, valine, isoleucine and iso-valine. The (%) stabilization for Cu^{2+} shows a somewhat smaller value with the *try* systems, which may perhaps be due to its tendency to prefer a square planar configuration.

Another significant aspect of the interaction seems to be the nature of the metal ion which plays the role of a bridge in the stacked biligand complexes. The geometry of the complex and the mode of bonding of the amino acid (through the two equatorial or one equatorial and one axial positions) may also affect the extent of interaction. In the present case stacking interaction has been noticed with all the metal ions under study (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+}) but by and large greater interaction occurs with Cu^{2+} . A recent report (Sigel *et al* 1985) on such interactions with phenyl acetate (or propionate) also shows the sequence $\text{Cu}^{2+} > \text{Zn}^{2+}$.

It may reasonably be concluded from the present studies that in the biosystems (biligand complexes of the type metal ion/enzyme/ATP, etc.) the properties of ternary complexes may be, to a good extent, the consequence of stacking interactions.

Acknowledgements

The senior author (MCS) expresses his thanks to the CSIR, New Delhi, for financial assistance, and the second author (SB) thanks them for a fellowship. Our thanks are due to the Head of our department for encouragement.

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An approximate theory of large molecules and molecular complexes[†]

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MS received 31 October 1986

Abstract. We present here an approximate *ab initio* formalism where a large molecule is treated in terms of its small subunits in such a way that both the integral generation and energy minimization problems are simplified. In this approach one can concentrate on one part of a molecular system and thus tailor the theoretical analysis to observations relating to this part of the system only.

Keywords. *Ab initio* theory; large molecules.

1. Introduction

All molecular systems in their ground state are known to consist of smaller subunits that, despite varying degrees of interaction, retain their identity to a large extent. This fact is of immense importance in a theoretical treatment of large molecules and has been utilized by various authors (Christoffersen and Maggiora 1969; Diner *et al* 1970; Christoffersen 1972; Shipman and Christoffersen 1973; Davis *et al* 1974; Pullman and Bethod 1978). This general characteristic allows one to break up the problem into a set of small steps involving these subunits. Theoretically speaking, this implies that one can set up meaningful equations relating to the local behaviour of a subunit even though the other parts of the molecule are only approximately described.

An actual rigorous development of a computational scheme for treating the subunits of a molecular system individually is, however, a non-trivial problem. The approaches in vogue in this area are of three kinds. While all three rely on reducing the basis set burden to minimal sets, the molecular-fragments approach (Christoffersen and Maggiora 1969; Christoffersen 1972; Shipman and Christoffersen 1973; Davis *et al* 1974) performs a conventional SCF and/or CI once the basis is selected. The Perturbation-CI with Localized Orbitals (PCILO) approach (Diner *et al* 1970) assumes a starting wavefunction that depends on bond orbitals, a concept of limited validity (particularly for complex systems). The molecular electrostatic potential model (Pullman and Bethod 1978) does not allow (at least explicitly) any scope for reoptimization of the parts of the system being replaced by such potentials.

We shall, in what follows, develop a formalism that allows one to handle a large molecule part by part. This implies that, no matter how large the system is, one can

[†] NCL Communication Number 3991.

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use this approach to get meaningful and accurate information on any part of the system.

2. A new scheme of integral management

What we propose to achieve here is an unconventional scheme by virtue of which one obtains an *ab initio* energy expression that uses segmented integral sets over basis functions spanning a given system.

First consider the energy expression. Exactly what form this takes depends on the nature of the wavefunction. Let us consider first a set of orbitals $\{\phi_{ap}\}$, a , denoting a molecular fragment which can be simply one of the constituent atoms. We shall denote the molecular orbitals as $\{\psi_i\}$ and assume them to be orthonormal and have the 'LCAO' form:

$$|i\rangle \equiv \psi_i = \sum_{a,p} c_{ap}^{(i)} \phi_{ap}. \quad (1)$$

In terms of the MO we shall assume an energy expression of the form,

$$E = \sum_i n_i h_i + \frac{1}{2} \sum_{i,j} n_i n_j (v_{ij}^J J_{ij} - v_{ij}^K K_{ij}), \quad (2)$$

where n_i are the occupancies, v_{ij}^J and v_{ij}^K are the vector-coupling coefficients,

$$\begin{aligned} h_i &= \langle i | h | i \rangle \\ J_{ij} &= \iint |\phi_i(\mathbf{r})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\phi_j(\mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}' \\ K_{ij} &= \iint \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}) \phi_i(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (3)$$

This 'diagonal' form of energy, though restricted, corresponds to many valid and accurate wavefunctions. Given (2), we shall indicate how, in general, one can reduce its evaluation to that of terms relating to fragments. Consider the one-electron terms:

$$\begin{aligned} h_i &\equiv \langle i | h | i \rangle \\ &= \sum_{pq,a} c_{ap}^{(i)} c_{aq}^{(i)} \langle ap | h | aq \rangle \\ &\quad + \sum_{pq, a \neq b} c_{ap}^{(i)} c_{bq}^{(i)} \langle ap | h | bq \rangle. \end{aligned} \quad (4)$$

For large molecular systems even within the conventional *ab initio* framework where all the necessary integrals are calculated accurately and are readily available, the calculation of h_i (as well as other terms of the energy) is facilitated by blocking the integrals $\langle ap | h | bq \rangle$ in terms of the blocks $B = [a, b]$, where a, b are individual fragments. Introducing the block index B and the corresponding differential

overlap $\rho_{B,pq} = \phi_{ap} \phi_{bq}$ and the density matrix element $D_{B,pq}^{(ij)}$, one can rewrite the one-electron matrix element as

$$h_i = \sum_B \sum_{pq} h_{B,pq} D_{B,pq}^{(ii)}, \quad (5)$$

or using matrix notation,

$$\mathbf{h} = \mathbf{h}^+ \mathbf{D}^{(ii)}. \quad (6)$$

The two-electron Coulomb repulsion terms can similarly be written in terms of the blocked J-supermatrix as

$$J_{ij} = \sum_{B, B'} \sum_{pq, rs} D_{B,pq}^{(ii)} \mathcal{G}_{Bpq, B'rs} D_{B'rs}^{(jj)}, \quad (7)$$

or in matrix notation,

$$J_{ij} = \mathbf{D}^{(ii)} \mathbf{J} \mathbf{D}^{(jj)}. \quad (8)$$

The exchange integrals will be expressed in terms of the supermatrix integrals as follows:

$$K_{ij} = \sum_{B, B'} \sum_{pq, rs} c_{ap}^{(i)} c_{a'r}^{(i)} c_{bq}^{(j)} c_{b's}^{(j)} \mathcal{G}_{Bpq, B'rs} \quad (9)$$

where $B = [ab]$ and $B' = [a'b']$. The greatest advantage that one can derive from this fragment-based blocking of integrals is by making sure that all the elements of an individual blocked supermatrix fit into the core. This implies that the blocks themselves must not be too large. As we shall see in the illustrations given below, this condition will be satisfied for many problems.

For large molecules it is essential to approximate the potential of distant blocks. A 'point-charge' model of the following description should be adequate in many cases. Assume that some of the blocks do not have appreciable differential overlap between the orbitals of its constituent fragments. These blocks clearly disappear from our energy expression as given by (5), (6) and (7). Furthermore for calculating the Coulomb integrals between the blocks $B = [ab]$ and $B' = [a'b']$, for which any of $[aa']$, $[ab']$, $[ba']$ or $[bb']$ has vanishing differential overlap. We use the approximation:

$$\rho_{Bpq} \cong S_{B,pq} \delta(\mathbf{r} - \mathbf{R}_{Bpq}), \quad (10)$$

where $\mathbf{R}_{B,pq}$ is a point (lying on the line joining the centres of the functions p and q) where $|\rho_{B,pq}|$ attains its maximum. In this approximation J_{ij} takes the form:

$$J_{ij} \cong \sum_{B, B'} \sum_{pq, rs} \frac{S_{Bpq} S_{B'pq} D_{Bpq}^{(ii)} D_{B'rs}^{(jj)}}{|\mathbf{R}_{Bpq} - \mathbf{R}_{B'rs}|} \quad (11)$$

Clearly (11) will hold only for large $|\mathbf{R}_{Bpq} - \mathbf{R}_{B'rs}|$.

3. A new ansatz of wavefunction of large molecular systems

The basic problem of treating a large molecular system by *ab initio* means is the fact that each molecular orbital spreads out over all the centres leading to the appearance of large matrices and supermatrices. It is also frequently true that the wavefunctions expressed in such molecular orbitals are not size-consistent and a monumental effort is needed in terms of configuration-mixing in order to 'dissociate' them properly.

One should, however, realize that this behaviour of molecular orbitals is more a mathematical artifact than reality; the orbitals spread out because of orthogonality and symmetry requirements. In any event a localization of the molecular orbitals can always be carried out, although this also implies that the wavefunctions using such orbitals are expanded in order to retain the same degree of accuracy. We present here an ansatz that depends on a special approximate treatment of the local orbitals. We first decouple the bond orbitals by introducing pair functions such as

$$\psi_{12} = a\phi_1^2 + b(\phi_1\phi_2)_0 + c\phi_2^2, \quad (12)$$

where ϕ_1 and ϕ_2 are the orbitals, suitably orthogonalized and belonging to the fragments M_1 and M_2 respectively, that participate in the bond. The notation $(\phi_1\phi_2)_0$ implies singlet coupling:

$$(\phi_1\phi_2)_0 = (2)^{-\frac{1}{2}} (\phi_1\alpha\phi_2\beta - \phi_1\beta\phi_2\alpha). \quad (13)$$

The main objective of the above construction is to be able to derive fragment-wise contributions to the total energy that can be independently optimized. To illustrate this let us consider a molecule consisting only of the fragments M_1 and M_2 and that there is only a single bond between them defined by the pair function ψ_{12} , all other orbitals being doubly-occupied. The matrix elements are:

$$\begin{aligned} H_{11} &= \langle \phi_1 | 2h_{\text{eff}} + J_1^{\text{op}} | \phi_1 \rangle \\ H_{22} &= \langle \phi_1 | h_{\text{eff}} + J_2^{\text{op}} + K_2^{\text{op}} | \phi_1 \rangle + \langle \phi_2 | h_{\text{eff}} | \phi_2 \rangle \\ H_{33} &= \langle \phi_2 | 2h_{\text{eff}} + J_2^{\text{op}} | \phi_2 \rangle \\ H_{21} &= 2^{\frac{1}{2}} \langle \phi_1 | h_{\text{eff}} + J_1^{\text{op}} | \phi_2 \rangle \\ H_{31} &= K_{12} \equiv \langle \phi_1 | K_2^{\text{op}} | \phi_1 \rangle \\ H_{32} &= 2^{\frac{1}{2}} \langle \phi_1 | h_{\text{eff}} + J_2^{\text{op}} | \phi_2 \rangle \end{aligned} \quad (14)$$

In the above h_{eff} consists of potentials generated by the occupation of the orbitals other than ϕ_1 and ϕ_2 :

$$h_{\text{eff}} = -\frac{1}{2} \nabla^2 + \sum_I V_I + \sum_i' (2J_i^{\text{op}} - K_i^{\text{op}}), \quad (15)$$

where summation over I runs over all the nuclei, that over i goes over all the occupied orbitals except ϕ_1 and ϕ_2 , $\{J_i^{\text{op}}\}$, $\{K_i^{\text{op}}\}$ being the Coulomb and exchange operators corresponding to the orbitals $\{\phi_i\}$.

Next we introduce a 'truncated overlap' concept as follows: We assign sets of basis functions spanning individual fragments. In general the functions of one fragment have non-zero overlap with those of the neighbouring fragments. However, the contribution of the overlaps falls off rapidly, roughly as the square of

the overlaps of individual orbitals multiplied by their occupancy in their respective fragments. Thus one can devise different levels of accuracy on the basis of a cut-off parameter below which all inter-fragment overlaps are set to zero. In such approximation the orthogonalization of orbitals on one fragment to those on the other will use only a truncated overlap matrix of a much smaller dimension than the full-blown one. Let the orbitals $\phi_i^{(1)}$ and $\phi_j^{(2)}$ centred on the fragments M_1 and M_2 be written as:

$$\begin{aligned}\phi_i^{(1)} &= \sum c_{ip}^{(1)} \chi_p^{(1)} \\ \phi_j^{(2)} &= \sum c_{jp}^{(2)} \chi_p^{(2)}\end{aligned}\quad (16)$$

These will have a net overlap given by

$$\langle \phi_i^{(1)} | \phi_j^{(2)} \rangle = c_{i1}^{(1)} c_{j1}^{(2)} S_{11}^{(12)}, \quad (17)$$

where $S_{11}^{(12)} = \langle \chi_1^{(1)} | \chi_1^{(2)} \rangle$, provided only the functions $\chi_1^{(1)}$ and $\chi_1^{(2)}$ overlap appreciably. Obviously the easiest way to achieve orthogonalization is to include in the sets $\{\chi_p^{(1)}\}$ and $\{\chi_p^{(2)}\}$ the functions $\chi_1^{(2)}$ and $\chi_1^{(1)}$ respectively. Rewriting $\phi_i^{(1)}$ and $\phi_j^{(2)}$ as

$$\begin{aligned}\phi_i^{(1)} &= \sum c_{ip}^{(1)} \chi_p^{(1)} + c_{i1}^{(2)} \chi_1^{(2)} \\ \phi_j^{(2)} &= \sum c_{jp}^{(2)} \chi_p^{(2)} + c_{j1}^{(1)} \chi_1^{(1)}\end{aligned}\quad (18)$$

we have

$$\langle \phi_i^{(1)} | \phi_j^{(2)} \rangle = \sum_{p,q=1}^2 c_{i1}^{(p)} c_{j1}^{(q)} S'_{pq}, \quad (19)$$

where the truncated overlap-matrix is given by:

$$S'_{pq} = \langle \chi_1^{(p)} | \chi_1^{(q)} \rangle. \quad (20)$$

We shall describe below how the above approach brings in considerable simplifications in connection with some typical bonding situations. Before that we consider the question of wavefunction optimization in the context of the present ansatz.

4. Wavefunction optimization

Once the Hamiltonian matrix along with all the basic matrices and supermatrices are in place, we concern ourselves with the optimization of the wavefunction. There are three levels of optimization to be distinguished. First consists of solving the secular equation for the coefficients a , b and c . Secondly, the orbital-vectors of a given fragment are to be optimally rotated amongst themselves. Finally the occupied orbitals are to be mixed with the virtual orbitals belonging to the same fragment. In order to optimize the mixing of the occupied orbitals of the fragment M_1 we use the criterion obtained from the multi-configuration self-consistent field

(MCSCF) formulation. If $\mathbf{e}_i^{(1)}$ and $\mathbf{c}_j^{(1)}$ are properly optimized orbital-vectors belonging to the fragment M_1 , they must satisfy (Hinze 1974):

$$\mathbf{c}_i^{(1)+}(\mathbf{F}_i^{(1)} - \mathbf{F}_j^{(1)})\mathbf{c}_j^{(1)} + \mathbf{c}_j^{(1)+}\mathbf{f}_i^{(1)} - \mathbf{c}_i^{(1)+}\mathbf{f}_j^{(1)} = 0, \quad (21)$$

where $\mathbf{F}_i^{(1)}$ and $\mathbf{F}_j^{(1)}$ are the corresponding Fock operators, $\mathbf{f}_i^{(1)}$ and $\mathbf{f}_j^{(1)}$ being the respective 'inhomogeneities':

$$\Delta_i^{(1)} \equiv \mathbf{F}_i^{(1)}\mathbf{c}_i^{(1)} + \mathbf{f}_i^{(1)} - \left(\sum_j \varepsilon_{ij}^{(1)} \mathbf{S}^{(1)}\mathbf{c}_j^{(1)} + \sum_j \varepsilon_{ij}^{(2)} \mathbf{S}'\mathbf{c}_j^{(2)'} \right) = 0, \quad (22)$$

where $\varepsilon_j^{(2)'}$ is the 'truncated' part of $\mathbf{c}_j^{(2)}$.

Turning to the question of optimization of the orbitals by mixing them with the virtual orbitals of the same fragment, we consider the Fock equations, themselves: We apply a Newton-Raphson type procedure (Wahl 1977):

$$\begin{aligned} & \left[\mathbf{F}_i^{(1)} - \sum_j (|\mathbf{S}\mathbf{c}_j^{(1)}\rangle\langle\mathbf{F}_i^{(1)}\mathbf{c}_j^{(1)}| + |\mathbf{F}_i^{(1)}\mathbf{c}_j^{(1)}\rangle\langle\mathbf{S}\mathbf{c}_j^{(1)}|) \right. \\ & \quad - \sum_j (|\mathbf{S}'\mathbf{c}_j^{(2)'}\rangle\langle\mathbf{F}_i^{(1)'}\mathbf{c}_j^{(2)'}| + |\mathbf{F}_i^{(1)'}\mathbf{c}_j^{(2)'}\rangle\langle\mathbf{S}'\mathbf{c}_j^{(2)'}|) \\ & \quad \left. - \varepsilon_i \mathbf{S}^{(1)} \right] \delta\mathbf{c}_i^{(1)} = -\Delta_i^{(1)}, \end{aligned} \quad (23)$$

and require that $\delta\mathbf{c}_i^{(1)}$ are orthogonal to the orbitals $\{\mathbf{c}_j^{(2)}\}$ through the truncated overlap matrix $\mathbf{S}'$.

5. Specific applications

We apply the above formulation to two different kinds of systems, those characterized by covalent and coordination bonding. We restrict ourselves to relatively small systems. However, the extension to larger systems will be seen to be straightforward. We do not attempt here to present any numerical tests, deferring them to a later report.

5.1 Covalent-bonded systems

We shall restrict ourselves to a simple covalent structure such as ethane consisting of two components (CH_3) bonded by a two-electron bond. We choose the wavefunction as:

$$\psi_{\text{tot}} = \tilde{A} \psi_1 \psi_2 [a \phi_1^2 + b(\phi_1 \phi_2)_0 + c \phi_2^2], \quad (24)$$

where ψ_1 , ψ_2 are composed of the closed-shell orbitals representing the CH-bonds and ϕ_1 , ϕ_2 the localized orbitals taking part in the C-C bond. Denoting the CH_3 fragments by the symbols M_1 and M_2 , the blocks are $[M_1 M_1]$, $[M_1 M_2]$ and $[M_2 M_2]$. However, using the 'truncated overlap-matrix' idea, the block $[M_1 M_2]$ is eliminated automatically by introducing the functions that overlap between M_1 and M_2 in each of the blocks $[M_1 M_1]$ and $[M_2 M_2]$. This is easily shown as follows. The part of energy that depends on ϕ_1 and ϕ_2 , when the orbitals are expanded in their respective fragment basis sets:

$$\begin{aligned}
\varepsilon_{12} = & a^2 \mathbf{D}_1^+ (2\mathbf{h}_{\text{eff}} + \mathcal{J} \mathbf{D}_1) \\
& + b^2 [\mathbf{D}_1^+ \{\mathbf{h}_{\text{eff}} + (\mathcal{J} + \mathcal{K}) \mathbf{D}_2\} + \mathbf{D}_2^+ \mathbf{h}_{\text{eff}}] \\
& + c^2 \mathbf{D}_2^+ (2\mathbf{h}_{\text{eff}} + \mathcal{J} \mathbf{D}_2) \\
& + 2ab \, 2^{\frac{1}{2}} \mathbf{D}_{12}^+ (\mathbf{h}_{\text{eff}} + \mathcal{J} \mathbf{D}_1) \\
& + 2bc \, 2^{\frac{1}{2}} \mathbf{D}_{12}^+ (\mathbf{h}_{\text{eff}} + \mathcal{J} \mathbf{D}_2) \\
& + 2ac \mathbf{D}_1^+ \mathcal{K} \mathbf{D}_2
\end{aligned} \tag{25}$$

where ϕ_i is represented by the vector $\mathbf{c}_i$,

$$\mathbf{h}_{\text{eff}} = \mathbf{h} + \sum'_{i \in M_1, M_2} (2\mathcal{J} \mathbf{D}_i - \mathcal{K} \mathbf{D}_i), \tag{15'}$$

the summation excluding $\phi_1, \phi_2, \{\mathbf{D}_i \equiv \mathbf{c}_i \mathbf{c}_i^+\}$ are the 'diagonal' density matrices and $\mathbf{D}_{12} \equiv \frac{1}{2}(\mathbf{c}_1 \mathbf{c}_2^+ + \mathbf{c}_2 \mathbf{c}_1^+)$. It is immediately seen that the terms $\mathbf{D}_{12}^+ \mathcal{J} \mathbf{D}_1, \mathbf{D}_{12}^+ \mathcal{J} \mathbf{D}_2$ use integrals of either the block $[M_1 M_1]$ or $[M_2 M_2]$. Also one can write, using the approximation in (10),

$$\begin{aligned}
\mathbf{D}_1^+ \mathcal{J} \mathbf{D}_2 = & (\mathbf{D}_2')^+ \mathcal{J} \mathbf{D}_1 + (\mathbf{D}_1')^+ \mathcal{J} \mathbf{D}_2 - (\mathbf{D}_1')^+ \mathcal{J} \mathbf{D}_2' \\
& + \sum_{pq, rs} ' \frac{S_{pq} S_{rs} c_{1p} c_{1q} c_{2r} c_{2s}}{|R_{pq} - R_{rs}|},
\end{aligned} \tag{26}$$

and

$$\mathbf{D}_1^+ \mathcal{K} \mathbf{D}_2 = (\mathbf{D}_1')^+ \mathcal{K}' \mathbf{D}_2'.$$

The summation over pq, rs excludes the 'overlapping' basis functions. All the $\mathcal{J}$ and $\mathcal{K}$ integrals required belong to either block $[M_1 M_1]$ or $[M_2 M_2]$.

It is easy to see how one can generalize this approach to, for example, the straight-chain hydrocarbons in which case our wavefunctions will look like:

$$\begin{aligned}
\psi_{\text{tot}} = & \tilde{A} \psi_1 \psi_2 \psi_3 \dots \times [a_{12} \phi_1^2 + b_{12} (\phi_1 \phi_2)_0 + c_{12} \phi_2^2] \\
& \times [a_{23} \psi_2^2 + b_{23} (\psi_2 \psi_3)_0 + c_{23} \psi_3^2] \times \dots,
\end{aligned} \tag{27}$$

where $(\phi_1, \phi_2), (\psi_2, \psi_3)$ etc. are the pairs forming the bonds.

5.2 Coordination-bonded systems

We shall consider in this category those bonds that are characterized by the following feature: There is a central atom (usually a transition metal) that binds together several ligands around itself by virtue of a 'sharing' of charge between its valence-orbitals and those on the ligands. Consider, for example, the coordination complex $\text{K}_3\text{Fe}(\text{CN})_6$. We construct the wavefunction in the following way: First we strip each potassium of its valence electron, donating the latter to the CN ligands. The potassium ions will serve only as charge centres yielding a potential field. Traditionally the wavefunction is constructed in an 'aufbau' fashion by distributing the 65 valence electrons into 32 doubly-occupied orbitals and one singly-occupied orbital. The single-determinant wavefunction that follows is then optimized in a semi-empirical framework (Reschke 1979). No *ab initio* work exists in the literature

(except those based on $X \alpha$ -techniques) to the best knowledge of the present authors.

Taking advantage of the very weak overlap of the CN^- -ligands with one another, we propose here a different kind of wavefunction. We construct the wavefunction in the following form (assuming that K^+ ions provide only potential fields and no additional electrons):

$$\begin{aligned} \psi_{\text{tot}} = & \tilde{A}(\text{Fe} - \text{core})(\Pi_i \psi_{\text{CN}^+, i}) \phi_4^2 \phi_5^2 \phi_6 \phi_{\text{CN}4}^2 \phi_{\text{CN}5}^2 \phi_{\text{CN}6}^2 \times \\ & [a_1 \phi_1^2 + b_1(\phi_1 \phi_{\text{CN}1})_0 + c_1 \phi_{\text{CN}1}^2] \times \dots \\ & [a_2 \phi_2^2 + b_2(\phi_2 \phi_{\text{CN}2})_0 + c_2 \phi_{\text{CN}2}^2] \times \\ & [a_3 \phi_3^2 + b_3(\phi_3 \phi_{\text{CN}3})_0 + c_3 \phi_{\text{CN}3}^2], \end{aligned} \quad (28)$$

where ψ_{CN^+} are the individual CN^+ wavefunctions, $\phi_i \equiv \phi_{\text{Fe}i}$, $i = 1, 2, \dots, 6$ are the iron orbitals and $\phi_{\text{CN}i}$, $i = 1, 2, \dots, 6$ are the openshell CN-orbitals. This wavefunction is based on the model of 'back-donation' where three of the CN^- -ligands actually form two-electron bonds with the three valence electrons on the iron. Of course any three ligands other than those used in (28) qualify for this. But because of negligible overlap between the CN ligands such resonant wavefunctions do not contribute significantly to the energy especially since we are principally interested only in the description of the electrons populating the Fe-orbitals.

Upon identifying the fragments as the Fe atom and the six CN-ligands, we note that only 13 blocks (seven diagonal and six off-diagonal) lead to non-negligible integrals assuming that orbitals on different CN-ligands do not overlap. The variational part of the total energy (i.e. those terms that contain the Fe and CN^- valence orbitals) is given by

$$\begin{aligned} \epsilon_{\text{val}} = & \frac{1}{2} \sum_{A=\text{CN}, \text{Fe}} \sum_{i=1}^6 n_{Ai} \mathbf{D}_{Ai}^+(\mathbf{h}_{\text{eff}} + \mathbf{F}_i^0) \\ & + \sum_{i=1}^3 [a_i^2 \mathbf{D}_{\text{Fe}i} \mathcal{J} \mathbf{D}_{\text{Fe}i} + b_i^2 \mathbf{D}_{\text{Fe},i}^+(\mathcal{J} + \mathcal{K}) \mathbf{D}_{\text{CN},i} + c_i^2 \mathbf{D}_{\text{CN},i}^+ \mathcal{J} \mathbf{D}_{\text{CN},i}] \\ & + 2 \sum_{i=1}^3 [(a_i + c_i) b_i 2^{\frac{1}{2}} \mathbf{c}_{\text{Fe}i}^+ \mathbf{F}_i^0 \mathbf{c}_{\text{CN}i} + a_i c_i \mathbf{D}_{\text{CN}i}^+ \mathcal{K} \mathbf{D}_{\text{Fe}i}] \\ & + 2 \times 2^{\frac{1}{2}} \sum_{i=1}^3 \mathbf{c}_{\text{Fe}i}^+(a_i b_i \mathcal{J} \mathbf{D}_{\text{Fe}i} + c_i b_i \mathcal{J} \mathbf{D}_{\text{CN}i}) \mathbf{c}_{\text{CN}i}, \end{aligned} \quad (29)$$

$$n_{Ai} = 2, A = \text{Fe or CN}, i = 4, 5, 6$$

$$n_{\text{Fe}i} = 2a_i^2 + b_i^2, n_{\text{CN}i} = 2c_i^2 + b_i^2, i = 1, 2, 3$$

$$\mathbf{D}_{Ai} = \mathbf{c}_{Ai} \mathbf{c}_{Ai}^+$$

$$\mathbf{F}_i^0 = \mathbf{h}_{\text{eff}} + \sum_{B=\text{CN}, \text{Fe}} \sum_{j \neq i} n_{Bj} (\mathcal{J} - \frac{1}{2} \mathcal{K}) \mathbf{D}_{Bj}. \quad (30)$$

Again using the argument from the previous example one can simplify the evaluation of all the terms such that they involve only the integrals belonging to individual fragments (i.e. only the seven diagonal blocks).

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***Ab initio* calculations of fundamental frequencies for isomeric difluorobenzenes**

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MS received 29 January 1987

Abstract. *Ab initio* computations of harmonic frequencies for the three isomeric difluorobenzenes have been carried out using the MO technique with split valence 3-21 G basis set. The computed frequencies have been compared with the experimental frequencies. The computed frequencies have been scaled with empirical scale factors in order to correct for the systematic errors originating in the limitations of the theoretical model. It was found necessary to use different scaling factors for the planar and non-planar modes.

Keywords. Isomeric difluorobenzenes; harmonic frequencies; molecular orbital technique.

1. Introduction

The accurate prediction of vibrational spectra of polyatomic molecules has been one of the goals of quantum theoretical studies. In recent years, *ab initio* molecular orbital theory has become a powerful tool for the calculation of vibrational frequencies of polyatomic molecules (Pulay 1981). Most of these studies are based on the method developed by Pulay (1969, 1977) in which forces acting on the nuclei for a molecular structure slightly displaced from its equilibrium configuration are directly calculated. The second derivatives of the potential energy with respect to the positional coordinates of the nuclei are then obtained numerically. Techniques and computer programmes featuring direct analytical evaluation of the second derivatives of the Hartree-Fock energy with respect to the nuclear coordinates have also been developed and shown to be practical (Pople *et al* 1979; Thomsen and Swanston 1973).

It is now realized that calculations employing split valence basis sets may yield vibrational frequencies which agree well with experimental values (after being scaled) as regards their general behaviour even though calculated values are usually 10–12% higher (Pulay and Meyer 1971; Pulay and Meyer 1974; Pople *et al* 1981; Wiberg and Wendoloski 1984). The calculated frequencies are often adjusted via simple scaling procedures so as to give a 'best fit' to the experimental vibrational

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frequencies. Two scaling procedures are in use. One of these (Pople *et al* 1981) directly scales the calculated frequencies while the second procedure scales the various force constants (Pulay and Meyer 1974). Scaling of the force constants grants us more flexibility in checking/modifying the vibrational assignments, especially if data from one molecule are to be used for other similar molecules. The direct scaling of the frequencies is also often used, since effects due to electron correlation, anharmonicity corrections etc. are not known well enough. Pople *et al* (1979) have pointed out that the whole concept of empirical scaling is of course conceptually unsatisfactory and is continued only as a practical necessity.

The present article reports the *ab initio* computation of the harmonic vibrational frequencies of the three isomeric difluorobenzenes using the HF/3-21 G basis set. A CNDO/2 study of the out-of-plane vibrations of these molecules has been made earlier by Torok *et al* (1976). It has already been noted by Pople *et al* (1981) that the use of the HF/3-21 G basis set provides accuracy comparable to the improved basis set HF-6-31 G* and is also less expensive.

2. Method of calculation

The vibrational frequencies have been calculated at Hartree-Fock level using 3-21 G basis set (Binkley *et al* 1979). Let the system consists of N nuclei having $3N$ nuclear coordinates. The energy E is calculated as a function of the $3N$ nuclear coordinates $x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N$. Let us denote these by R_i ($i = 1, 2, 3, \dots, 3N$). If m_i be the mass associated with the coordinate R_i so that $m_1 = m_2 = m_3$ is the mass corresponding to the first nucleus and so on and r_i be a small change in R_i , then the classical equation of motion is

$$m_i \ddot{r}_i = - \sum_j f_{ij} r_j, \quad (1)$$

f_{ij} being the force constants. In terms of mass weighted force constants,

$$f'_{ij} = f_{ij} m_i^{-1/2} m_j^{1/2} \quad (2)$$

and (1) can be written as

$$\ddot{r}_i = - \sum_j f'_{ij} r_j. \quad (3)$$

For a normal mode atomic displacements have the form

$$r_i = a_i \exp (2\pi \nu (-1)^{1/2} t), \quad (4)$$

and therefore, (3) reduces to

$$\sum_j f'_{ij} a_j = 4\pi^2 \nu^2 a_i, \quad (5)$$

where a_i are the amplitudes of the normal coordinates. The eigen-values $4\pi^2 \nu^2$ are obtained by diagonalizing the mass weighted force constants f'_{ij} . ν are the harmonic frequencies and the eigen vectors r_i give the amplitudes of the normal coordinates. Six of the $3N$ frequencies corresponding to the translational and the

rotational motions of the molecule will be zero and the remaining $3N-6$ frequencies will correspond to the internal vibrations. The force on the nuclei and the force constants are calculated by the first and second energy derivatives respectively, which are represented by the expressions

$$f_i = \frac{\partial E}{\partial R_i} \quad (6)$$

and

$$f_{ij} = \frac{\partial^2 E}{\partial R_i \partial R_j} \quad (7)$$

These quantities have been evaluated using a computer program developed by Pople *et al* (1979). However, the integral involved in the second derivatives of the energy has been obtained numerically because of computer storage problems. All calculations have been performed on a VAX-11/750 computer. The geometrical parameters used for the calculations of vibrational frequencies are: $r(\text{C}-\text{C}) = 1.397 \text{ \AA}$, $r(\text{C}-\text{H}) = 1.084 \text{ \AA}$, $r(\text{C}-\text{F}) = 1.350 \text{ \AA}$, $\angle \text{C}-\text{C}-\text{C} = \angle \text{H}-\text{C}-\text{C} = \angle \text{F}-\text{C}-\text{C} = 120^\circ$. An *ab initio* evaluation of the geometries of the fluorobenzenes with a discussion of the most reliable geometry has been given by Boggs *et al* (1982). However, since the above transformation (5) is valid at a stationary point of the energy surface, the use of a geometry optimised using a basis set other than the one used here (3-21 G) would not have any significance. Therefore, no effort was made to consider any geometry optimization.

3. Results and discussion

The computed harmonic frequencies together with the experimental frequencies (Pearce *et al* 1973; Eaton and Steele 1973; Eaton *et al* 1976; Varsanyi 1974) and the tentative assignments for *ortho*-, *meta*- and *para*-difluorobenzenes are presented in table 1.

The average value for the ratio $\nu_{\text{exp}}/\nu_{\text{cal}}$ considering all the frequencies was found to be 0.89 for the three molecules. Therefore, a scale factor of 0.89 may be proposed as correcting for the deficiencies in the SCF method as well as for the anharmonic nature of the experimental frequencies. A larger deviation is found between calculated and observed frequencies for the non-planar modes as compared to that for the planar modes and the computed non-planar frequencies usually have much higher magnitudes than the observed ones. Other workers (Wiberg and Wendolosky 1984) have also made similar observations. The average $\nu_{\text{exp}}/\nu_{\text{cal}}$ for planar frequencies was found to be 0.93 whereas for the non-planar frequencies it was 0.8. The use of a single scale factor of 0.89 for planar and non-planar frequencies gives an average error of 64 cm^{-1} whereas the use of two different scale factors of 0.93 and 0.80 gives an average error of only 28 cm^{-1} . Therefore, different scale factors of 0.93 and 0.80 are used for planar and non-planar frequencies respectively. The fact that the scale factors needed for out-of-plane modes are lower than those for the in-plane ones has been emphasized earlier by Pulay *et al* (1981) and indicates that a scaling of the calculated frequencies

Table 1. Theoretical and experimental vibrational frequencies (cm^{-1}) for *o*-, *m*- and *p*-difluorobenzenes with 3-21G basis set.

Molecules	Species	Theoretical Frequencies			Experimental frequencies	Vibrational assignments*	
		Cal.	Exp./Cal.	Scaled			
<i>o</i> -Di-fluoro-benzene		3275	0.941	3046	3081	$\nu(\text{C-H})$	(2)
		3257	0.935	3029	3045	$\nu(\text{C-H})$	(20b)
		1716	0.935	1596	1605	$\nu(\text{C}=\text{C})$	(8a)
		1674	0.904	1557	1514	$\nu(\text{C}=\text{C})$	(19b)
		1426	0.906	1326	1292	$\nu(\text{C-F})$	(7a)
		1342	0.948	1248	1272	$\nu(\text{C}=\text{C})$	(14)
		1139	1.011	1059	1152	$\beta(\text{C-H})$	(9a)
		1106	0.927	1029	1025	$\beta(\text{C-H})$	(18b)
		811	0.940	754	762	$\nu(\text{C-C})$	(1)
		641	0.886	596	568	$\alpha(\text{C-C-C})$	(6a)
		289	0.993	269	287	$\beta(\text{C-F})$	(15)
		3267	0.937	3038	3060	$\nu(\text{C-H})$	(20a)
		3243	—	3016	—	$\nu(\text{C-H})$	(7b)
		1733	0.934	1612	1618	$\nu(\text{C}=\text{C})$	(8b)
		1617	0.910	1504	1472	$\nu(\text{C}=\text{C})$	(19a)
	b_2	1432	0.875	1332	1253	$\beta(\text{C-H})$	(3)
		1339	0.901	1245	1206	$\nu(\text{C-F})$	(13)
		1216	0.907	1131	1103	$\beta(\text{C-H})$	(18a)
		951	0.901	884	857	$\alpha(\text{C-C-C})$	(12)
		587	0.930	546	546	$\alpha(\text{C-C-C})$	(6b)
		476	0.924	443	440	$\beta(\text{C-F})$	(9b)
		1183	0.785	946	929	$\gamma(\text{C-H})$	(17b)
		955	0.784	764	749	$\gamma(\text{C-H})$	(11)
	b_1	582	0.773	466	450	$\phi(\text{C-C-C-C})$	(16b)
		358	0.768	286	275	$\gamma(\text{C-F})$	(10a)
		1222	0.794	978	970	$\gamma(\text{C-H})$	(5)
		1082	0.776	866	840	$\gamma(\text{C-H})$	(17a)
	a_2	877	0.802	702	703	$\phi(\text{C-C-C-C})$	(4)
		659	0.892	527	588	$\phi(\text{C-C-C-C})$	(16a)
		237	0.827	190	196	$\gamma(\text{C-F})$	(10b)
<i>m</i> -Di-fluoro-benzene		3273	0.943	3044	3087	$\nu(\text{C-H})$	(2)
		3270	—	3041	—	$\nu(\text{C-H})$	(20a)
		3249	0.938	3022	3049	$\nu(\text{C-H})$	(7a)
		1725	0.930	1604	1605	$\nu(\text{C}=\text{C})$	(8a)
		1563	0.927	1454	1449	$\nu(\text{C}=\text{C})$	(19a)
		1466	0.871	1363	1277	$\nu(\text{C-F})$	(13)
		1174	0.908	1092	1066	$\beta(\text{C-H})$	(18a)
	a_1	1094	0.921	1017	1008	$\alpha(\text{C-C-C})$	(12)
		804	0.914	748	735	$\nu(\text{C-C})$	(1)
		580	0.903	539	524	$\alpha(\text{C-C-C})$	(6a)
		332	0.997	308	331	$\beta(\text{C-F})$	(9a)
		3262	0.949	3034	3096	$\nu(\text{C-H})$	(20b)
		1755	0.919	1632	1613	$\nu(\text{C}=\text{C})$	(8b)
		1645	0.906	1530	1490	$\nu(\text{C}=\text{C})$	(19b)
		1466	0.912	1363	1337	$\beta(\text{C-H})$	(3)
		1333	0.945	1240	1260	$\nu(\text{C}=\text{C})$	(14)
	b_2	1310	0.884	1218	1158	$\beta(\text{C-H})$	(9b)
		1140	0.982	1060	1120	$\beta(\text{C-H})$	(18b)

Table 1.

Molecules	Species	Theoretical Frequencies			Experimental frequencies	Vibrational assignments*	
		Cal.	Exp./Cal.	Scaled			
<i>p</i> -Di-fluoro-benzene	<i>b₁</i>	1027	0.929	955	954	$\nu(\text{C-F})$	(7b)
		572	0.899	532	514	$\alpha(\text{C-C-C})$	(6b)
		499	0.958	464	478	$\beta(\text{C-F})$	(15)
		1221	0.801	977	978	$\gamma(\text{C-H})$	(5)
		1135	0.749	908	850	$\gamma(\text{C-H})$	(17b)
		991	0.776	793	769	$\gamma(\text{C-H})$	(11)
		829	0.811	663	672	$\phi(\text{C-C-C-C})$	(4)
		569	0.805	455	458	$\phi(\text{C-C-C-C})$	(16b)
		286	0.804	229	230	$\gamma(\text{C-F})$	(10b)
		1131	0.777	906	879	$\gamma(\text{C-H})$	(17a)
	<i>a₂</i>	725	0.826	580	599	$\phi(\text{C-C-C-C})$	(16a)
		306	0.820	245	251	$\gamma(\text{C-F})$	(10a)
	<i>a_g</i>	3273	0.942	3044	3084	$\nu(\text{C-H})$	(2)
		1766	0.916	1642	1617	$\nu(\text{C=C})$	(8a)
		1405	0.886	1307	1245	$\nu(\text{C-F})$	(7a)
		1298	0.880	1207	1142	$\beta(\text{C-H})$	(9a)
		905	0.948	842	858	$\nu(\text{C-C})$	(1)
		500	0.902	465	451	$\alpha(\text{C-C-C})$	(6a)
		3256	0.948	3028	3088	$\nu(\text{C-H})$	(20a)
		1693	0.892	1574	1511	$\nu(\text{C=C})$	(19a)
		1412	0.858	1313	1285	$\nu(\text{C-F})$	(13)
		1105	0.916	1028	1012	$\beta(\text{C-H})$	(18a)
	<i>b_{1u}</i>	805	0.916	747	737	$\alpha(\text{C-C-C})$	(12)
		3271	0.926	3042	3028	$\nu(\text{C-H})$	(20b)
		1541	0.933	1433	1437	$\nu(\text{C=C})$	(19b)
		1226	0.989	1140	1212	$\nu(\text{C=C})$	(14)
	<i>b_{2u}</i>	1130	0.960	1051	1085	$\beta(\text{C-H})$	(18b)
		347	1.009	323	350	$\beta(\text{C-F})$	(15)
		3257	0.947	3029	3084	$\nu(\text{C-H})$	(7b)
		1684	—	1566	—	$\nu(\text{C=C})$	(8b)
	<i>b_{3g}</i>	1455	0.883	1353	1285	$\beta(\text{C-H})$	(3)
		717	0.886	667	635	$\alpha(\text{C-C-C})$	(6b)
		477	0.910	444	434	$\beta(\text{C-F})$	(9b)
		1210	0.779	968	943	$\gamma(\text{C-H})$	(17a)
	<i>a_u</i>	534	0.758	427	405	$\phi(\text{C-C-C-C})$	(16a)
		1037	0.771	830	800	$\gamma(\text{C-H})$	(10a)
		1199	0.774	959	928	$\gamma(\text{C-H})$	(5)
		858	0.807	686	692	$\phi(\text{C-C-C-C})$	(4)
	<i>b_{2g}</i>	446	0.841	357	375	$\gamma(\text{C-F})$	(10b)
		1057	0.788	846	833	$\gamma(\text{C-H})$	(17b)
		645	0.781	516	504	$\phi(\text{C-C-C-C})$	(16b)
		184	0.902	147	166	$\gamma(\text{C-F})$	(11)

*Numbers within parenthesis following each assignment correspond to mode of vibration (Wilson 1934).

ν : Stretching; β : in-plane bending; α : C-C-C angle bending; γ : out-of-plane bending; and ϕ : torsion about C=C bond.

may be more appropriate. It has also been observed that for planar frequencies $\Delta\nu$ is below 30 cm^{-1} for frequencies below 1100 cm^{-1} and below 70 cm^{-1} for frequencies above 1100 cm^{-1} . For the non-planar frequencies $\Delta\nu$ is below 30 cm^{-1} except for the 588 cm^{-1} frequency (mode-16a) in *o*-difluorobenzene and the 850 cm^{-1} frequency (mode-17b) in *m*-difluorobenzene.

The assignments of the fundamental frequencies for *o*-, *m*-, and *p*-difluorobenzenes presented in table 1 are based on the assignments made by earlier workers (Pearce *et al* 1973; Eaton and Steele 1973; Eaton *et al* 1976; Varsányi 1974) and are essentially identical to those given by Varsányi (1974) except for the cases discussed below.

For *o*-difluorobenzene, Varsányi (1974) has assigned the frequency 1272 cm^{-1} to the C-F stretching mode (7a). The *ab initio* results show that the normal mode corresponding to this frequency amplitude does not involve any movement of the fluorine atoms. Instead the *ab initio* calculated frequency 1426 cm^{-1} corresponding to the experimental frequency 1292 cm^{-1} which has earlier (Varsányi 1974) been assigned to the Kekule C=C stretching mode-14 does involve a displacement of fluorine atoms. Therefore, we now assign the observed frequencies 1272 and 1292 cm^{-1} to the C=C stretching mode-14 and the C-F stretching mode-7a respectively. This is consistent with their a_1 symmetry.

The two interesting and widely discussed vibrational modes in substituted benzenes are the ring breathing (mode-1) and the trigonal C-C-C angle bending (mode-12). In disubstituted benzenes the interaction of these vibrational modes with vibrational modes involving substituent(s) motions (usually C-X stretchings) gives rise to two observed frequencies, one in the region $750\text{--}825\text{ cm}^{-1}$ and the other in the region $990\text{--}1050\text{ cm}^{-1}$, both of which usually appear in the Raman spectrum with good intensities. One of these frequencies is usually attributed to the ring breathing or the C-C-C trigonal bending mode. The frequencies of magnitude 762 cm^{-1} and 1025 cm^{-1} observed as the strongest lines in the Raman spectrum of *o*-difluorobenzene are assigned to the ring breathing mode and the C-H in-plane bending modes, respectively (Varsányi 1974). The *ab initio* calculations show that the frequency 762 cm^{-1} involves just the radial motion of all atoms which is the characteristic nature of the ring breathing mode. On the other hand, the frequency 1025 cm^{-1} does not involve the displacement of any fluorine atoms nor of the corresponding carbon atoms. The earlier assignment (Varsányi 1974) of the frequency 1025 cm^{-1} to the C-H in-plane bending mode thus seems to be reasonably correct. The trigonal C-C-C angle bending mode assigned by Varsányi (1974) to a frequency at 857 cm^{-1} is also supported by our calculations.

The assignments for the *m*-difluorobenzenes are identical to those given by Varsányi (1974) and are supported by our computations.

We have noted that for frequencies above 1100 cm^{-1} the difference between the computed and the observed magnitudes is below 70 cm^{-1} . The same holds true for *p*-difluorobenzene also except for the two frequencies observed at 1212 cm^{-1} (mode- b_{1u}) and at 1285 cm^{-1} (mode- b_{2u}). These frequencies had been assigned to the C-F stretching (mode-13) and the C-C stretching (mode-14) vibrations, respectively. The corresponding calculated magnitudes for the modes 13 and 14 are 1412 and 1226 cm^{-1} which after scaling become 1313 and 1140 cm^{-1} respectively. Thus, if the earlier assignments are retained $\Delta\nu(\nu_{\text{cal}} - \nu_{\text{obs}})$ for the two cases are 101 and 145 cm^{-1} respectively which are far larger than $\Delta\nu^{\circ}\text{s}(\sim 70\text{ cm}^{-1})$ for other

frequencies above 1100 cm^{-1} . However, if we interchange the assignments of the observed frequencies $\Delta\nu$ is reduced to 72 and 28 cm^{-1} , respectively, well within the expected limit. Both the modes are infrared-active and the normal mode with the frequency 1285 cm^{-1} involves displacement of the fluorine atoms whereas the normal mode with the frequency 1212 cm^{-1} does not involve any displacement of F atoms. The interchange of assignments is thus justified and we assign the frequencies 1212 and 1285 cm^{-1} to the C=C stretching (mode-14) and to the C-F stretching (mode-13) respectively. The interchange of the assignments for these two frequencies seems to be justified by an additional experimental observation explained in the following paragraph.

The magnitudes of the six C=C stretching frequencies decrease in going from benzene- h_6 to benzene- d_6 and one would expect a similar pattern in going from *p*-difluorobenzene- h_4 to *p*-difluorobenzene- d_4 . In contrast, the magnitudes of the C-F stretching frequencies are not expected to be affected appreciably in going from $\text{C}_6\text{F}_2\text{H}_4$ to $\text{C}_6\text{F}_2\text{D}_4$. In the infrared spectrum of *p*-difluorobenzene- h_4 , two fundamentals were observed in the region $1200\text{--}1300\text{ cm}^{-1}$, namely, 1212 and 1285 cm^{-1} , whereas in the infrared spectrum of *p*-difluorobenzene- d_4 (Gates *et al* 1969) only a single fundamental at 1287 cm^{-1} was observed. It seems logical to assume that the frequency 1285 cm^{-1} in the normal compound corresponds to the frequency 1287 cm^{-1} in the deuterated compound and is a C-F stretching rather than a C=C stretching fundamental. In the infrared spectrum of *p*-difluorobenzene- d_4 the only frequency which may be correlated with the 1212 cm^{-1} of *p*-difluorobenzene- h_4 is 1133 cm^{-1} which can therefore be assigned to the C=C stretching mode.

4. Conclusions

The breathing mode is observed to decrease considerably in magnitude as compared to its magnitude (992 cm^{-1}) for benzene in all the three cases, whereas the trigonal C-C-C angle bending mode is observed to be reduced in magnitude for the *o*- and the *p*-isomers, but retains its magnitude (1008 cm^{-1}) in the *m*-isomer. Interestingly enough, the breathing mode has its lowest magnitude of 735 cm^{-1} and the trigonal bending mode its highest magnitude of 1008 cm^{-1} for the *m*-isomer whereas the breathing mode has its highest magnitude of 858 cm^{-1} and the trigonal bending mode has its lowest magnitude of 737 cm^{-1} for the *p*-isomer. Therefore, we may conclude that in the *m*-isomer the breathing mode mixes strongly with other modes whereas the trigonal bending mode mixes only slightly. On the other hand it seems that in the *p*-isomer the trigonal bending mode interacts strongly with other modes and it is the breathing mode which interacts only slightly. The magnitude of the Kekule C=C stretching mode is found to be in decreasing order on going from the *o*- to the *m*- to the *p*-isomer suggesting a decreasing mixing with other modes. Out of the two C-F stretching modes, one mode is always taken to correspond to mode-13 of benzene. This mode is observed to have magnitudes of 1206 , 1277 and 1285 cm^{-1} for the *o*-, *m*- and *p*-isomers, respectively. The other C-F stretching mode is described by the mode-7a in the *o*- and the *p*-isomers and as mode-7b in the *m*-isomer. The C-F stretching (mode-7a) for the *o*- and *p*-isomers is observed to have nearly equal magnitudes whereas for

Table 2.

Normal mode specification	<i>o</i> -Difluoro-benzene	<i>m</i> -Difluoro-benzene	<i>p</i> -Difluoro-benzene
C-F stretching	1292 (7a) 1206 (13)	954 (7b) 1277 (13)	1245 (7a) 1285 (13)
Ring breathing	762	735	858
Trigonal bending	857	1008	737
Kekula C=C	1272	1260	1212

the *m*-isomer (mode-7b) it is observed to have considerably reduced magnitude which may be due to its interaction with other C-F/ring modes. The frequencies corresponding to the two C-F stretchings, the ring breathing, the trigonal C-C-C angle bending and the Kekule C=C stretching modes are summarised in table 2.

Acknowledgements

The authors wish to thank Prof S N Thakur for some fruitful comments: The critical reading of the manuscript by Prof D K Rai is greatly appreciated. The willing and helpful cooperation of Dr A Sawaryn during the computation is gratefully acknowledged. OPS and JSY are also thankful to Prof P Pulay, E L University, Budapest, Hungary, and Dr J D Goddard, University of Guelph, Ontario, Canada, for some valuable discussions and suggestions. One of us (OPS wishes to thank Dr P P Singh, Principal, MLK (PG) College, Balrampur, for encouragement and the University Grants Commission, New Delhi, for a fellowship.

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Resonance Raman studies of tetraphenylporphinato manganese(III) chloride

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MS received 29 October 1986; revised 11 August 1987

Abstract. Resonance Raman spectra of Mn(III)TPPCl in different solvents as well as in KBr pellets have been obtained with laser excitations in different regions of the atypical absorption spectrum of the system. The selective enhancement of vibrational modes arising from different parts of the molecule under excitation in different absorption regions has been used to assign the electronic transitions of Mn(III)TPPCl. The strong absorption band at ~ 476 nm originates from a charge transfer transition between porphyrin and metal orbitals, while a weaker band at ~ 530 nm has been identified due to singlet-triplet (π, π^*) transitions. The present data do not provide distinct evidence for activation of the phenyl group modes under resonance Raman conditions indicating thereby that the phenyl groups may not be conjugated with the porphyrin macrocycle. Depolarization ratios for some isolated bands show dispersion with excitation wavelengths due to reduction of the chromophore symmetry.

Keywords. Resonance Raman scattering; Mn(III)-tetraphenylporphin; Raman studies of metalloporphyrins.

1. Introduction

Extensive studies on the physical and chemical properties of porphyrins and metalloporphyrins have been stimulated in recent years (Smith 1975; Drabkin 1978; Lee *et al* 1986), as they play important roles in many biological systems such as haemoglobin, myoglobin, chlorophylls etc.

The study of Mn(III) porphyrin complexes has been an area of growing research activity during recent years (Boucher 1972; Gaughan *et al* 1975; Asher and Sauer 1976; Shelnutt *et al* 1976; Spreer *et al* 1986). These complexes exhibit an atypical electronic absorption spectrum which is diagnostic of their unusual electronic structure. The metal orbitals in these systems have a much stronger influence on the ligand orbitals than in other systems; the metal-porphyrin π -mixing does not only alter the normal porphyrin (π, π^*) spectra, but also induces distinct new features in the absorption spectra. Many studies have been concerned with the nature of these extra features, yet their origin is not fully understood and many controversial reports exist in the literature. The intense band at ~ 476 nm has been ascribed to charge transfer transition (Boucher 1970, 1972; Gaughan *et al* 1975; Asher and Sauer 1976), charge-transfer mixed with (π, π^*) character (Shelnutt *et al* 1976; Gouterman 1978). The near IR bands have been ascribed to $d \rightarrow d$ transitions of the metal (Baker and Perumareddi 1970; Linder and Rowlands 1971), $d \rightarrow \pi$ charge-transfer transitions (Boucher 1970), triplet (π, π^*) transitions mixed

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with charge transfer character (Kobayashi *et al* 1973), while the bands III and IV have been associated with the (π, π^*) transitions and/or charge transfer transitions (Boucher 1970, 1972; Shelnett *et al* 1976). However, to our knowledge, no attempt has yet been made to understand the origin of a band around 530 nm in the absorption spectrum of tetraphenylporphinato manganese(III)chloride (Mn(III)TPPCL). Thus, the understanding of the electronic spectra of these complexes is still ambiguous and it is highly desirable to probe the electronic structure of their complexes in greater detail. In this respect, it is also necessary to elucidate the role of the external substituents in perturbing the basic electronic structure of the chromophore.

A variety of physical methods has been applied and has helped to achieve considerably deeper insight into these systems. More recently, the resonance Raman (RR) technique has been used by several workers to study these systems (Felton and Yu 1978; Asher 1981; Spiro 1983; Sarkar and Verma 1986; Kitagawa and Ozaki 1987).

It is clear from different studies that the modifications in the RR spectra produced by changes in peripheral substituents to porphyrin structure are induced mainly by changes in the porphyrin macrocycle and/or vibrational coupling among the vibrations of the side chains with the macrocycle, rather than conjugative effects. If the sidechain substituents form a conjugated system and perturb the electronic structure of the porphyrin macrocycle, then vibrations corresponding to the external substituents should show in the RR spectra. There are some studies which report the contribution of the peripheral substituents to the RR spectra of metalloporphyrins (Burke *et al* 1978; Choi *et al* 1982; Schick and Bocian 1983; Hofmann and Bocian 1984) while some other reports (Brunner and Sussner 1973; Ivanova and Berdyugin 1984; Sarkar and Verma 1986) do not support this view. The selective enhancement of the scattering cross-section for certain vibrational modes by excitation in different absorption regions may be of great help for assigning the electronic/vibrational states of the molecule. Moreover, since the depolarization ratio of Raman bands is a very sensitive function of porphyrin symmetry, dispersion of depolarization ratio with excitation frequency can provide detailed information about the symmetry of the system.

In this paper, we report the RR studies of Mn(III)TPPCL with different excitation wavelengths. Selective enhancement of certain vibrational modes arising due to excitation in different parts of the optical spectra has been used to assign the electronic transitions. Secondly, the intensity dependence of some modes, which have been previously ascribed to phenyl group modes, was monitored as a function of exciting frequency and the state of conjugation of the phenyl rings with the porphyrin macrocycle explored. Finally, the depolarization ratios of some isolated bands with different excitation wavelengths have been measured to provide information about the symmetry of the system.

2. Experimental

MnTPPCL was prepared by the standard procedure (Adler *et al* 1970). Free base TPP and MnCl_2 were refluxed in dimethyl formamide solution for about $1\frac{1}{2}$ hours. MnTPPCL was extracted with chloroform and washed with water to remove

unreacted MnCl_2 . The sample was further purified by column chromatography on silica gel. The Raman spectra in the solid form were obtained in KBr pellets in very low concentrations. Raman spectra were also obtained in the carbon disulphide (CS_2) and pyridine (Py) solutions at $\sim 10^{-4}$ M concentration. All the Raman spectra were recorded in 90° scattering geometry with a SPEX Ramalog 1403 triple monochromator equipped with a cooled RCA 31034 photomultiplier and photon counting arrangement. The spectrometer control and data processing were achieved with the help of a microprocessor based 'SPEX' datamate. Excitation wavelengths were provided by Spectra-Physics 165 Argon ion laser, 375 dye laser, Liconix He-Cd laser and Coherent (Innova 90 K) Krypton ion laser. The rotating cell technique was used for both solutions as well as KBr pellets to avoid local heating and decomposition of the samples. The spectra were calibrated with CCl_4 , helium and krypton lamp lines and the reported band positions are accurate to better than $\pm 2 \text{ cm}^{-1}$. To improve signal to noise ratio for weak features, 3 to 4 spectra were averaged.

3. Results and discussion

3.1 Results

The structure of Mn(III)TPPCL is shown in figure 1. Absorption spectra were recorded in different solvents such as carbon disulphide (CS_2), dichloromethane (CH_2Cl_2), benzene (Bz), and pyridine (Py). Figure 2 shows the absorption spectra of MnTPPCL in CS_2 and Py solutions and table 1 lists the absorption maxima obtained in all the above solvents. Bands are labelled following Boucher (Boucher 1972). The intensity patterns of the bands are rather similar in all the cases, although the intensity ratios differ. However, in Py solution, the relative intensities of the bands III and IV change and a new feature appears at $\sim 425 \text{ nm}$. Although the absorption maxima of different bands clearly vary in different solvents, there is no simple correlation by which they can be assigned to a particular type of transition based on expected solvent dependence.

RR spectra of MnTPPCL in KBr pellets with $\lambda_{\text{ex}} = 4765 \text{ \AA}$, $5309 \text{ \AA}$, $5831 \text{ \AA}$ and $6116 \text{ \AA}$ are displayed in figure 3a. Figure 3b gives the RR spectra of MnTPPCL in KBr pellets with $\lambda_{\text{ex}} = 4416 \text{ \AA}$, while figure 4a and 4b give the Raman spectra of MnTPPCL in CS_2 and C_2Cl_4 solutions with $\lambda_{\text{ex}} = 4765 \text{ \AA}$, $5840 \text{ \AA}$ and $6198 \text{ \AA}$. The locations of the laser lines for the pellet spectra have been shown in figure 2. The corresponding Raman frequencies in KBr pellets as well as in CS_2 solutions have been given in tables 2 and 3 respectively. The depolarization ratios of most of the bands have been measured. Almost all the bands have analogues in the RR spectra of FeTPP systems (Burke *et al* 1978; Schick and Bocian 1983; Hofmann and Bocian 1984) and have been assigned correspondingly with other known assignments. It is interesting to note that the lower frequency vibrations, i.e., below 500 cm^{-1} are enhanced mainly with the $4765 \text{ \AA}$ and $4416 \text{ \AA}$ excitations. This is the region where metal-ligand vibrations are expected to occur. Excitation in all other regions enhance the higher frequency vibrations, i.e., the vibrations related to the porphyrin macrocycle. For further confirmation that the lower frequency vibrations are related to metal, Raman spectra of MnTPPCL in Py solution have been

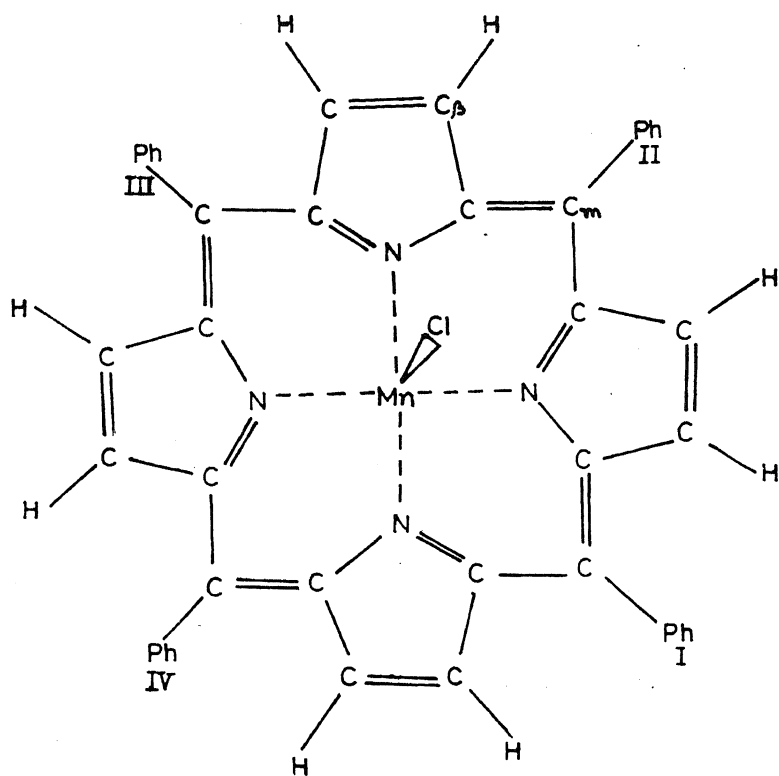


Figure 1. Structure of tetraphenylporphinato manganese(III)chloride. Ph denotes phenyl group.

Table 1. Absorption maxima (nm) for Mn(III)TPPCL in different solvents ($\sim 10^{-5}$ M concentration).

CS ₂	CH ₂ Cl ₂	Benzene	Pyridine
755	~758	~753	783
~698	~700	~700	713
675	675		685
620	614	616	605
583	578	578	570
530	525	530	523
476	468	472	470
			425
400	400	395	403
380	370	368	378

obtained. Figures 4a and 5 give a comparison of the Raman data obtained in different solvents. It is known that in Py solution the axial positions of Mn in the MnTPPCL are occupied by the Py molecules resulting in a shift of the Mn ion towards the porphyrin plane. This should obviously affect the metal-related vibrations. As can be seen from figures 4a and 5, the Raman spectra obtained in Py

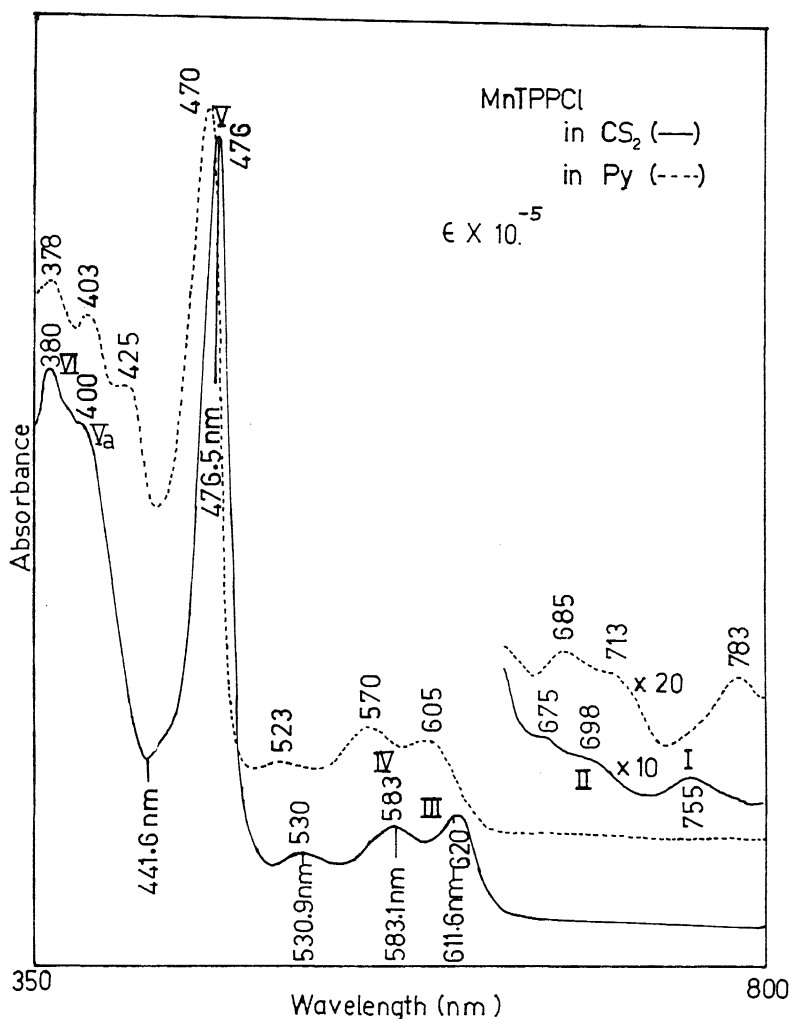


Figure 2. Absorption spectra of Mn(III)TPPCL ($\sim 10^{-5}$ M) in CS₂ (—) and in pyridine (-----) solutions.

solution differ markedly from the spectra obtained in CS₂ solution. A medium intensity band at 262 cm⁻¹ observed in CS₂ solution disappears in the spectra in Py solutions. The features appearing at 221 cm⁻¹ and 301 cm⁻¹ in CS₂ solutions shift to 227 and 293 cm⁻¹ respectively in Pyridine solutions. The relative intensities of the bands also change drastically.

The absence of the band at 262 cm⁻¹ in Py solution suggests that it is associated with the Mn-Cl stretching vibration. This assignment is consistent with previous work on related systems (Boucher 1970; Asher and Sauer 1976). From the observed shift in the 221 and 301 cm⁻¹ bands (CS₂) to 227 and 293 cm⁻¹ (Py), those features may be associated with Mn-nitrogen stretching and deformation modes respectively. The higher frequency spectra (500–1700 cm⁻¹) show somewhat similar features in the two solvents.

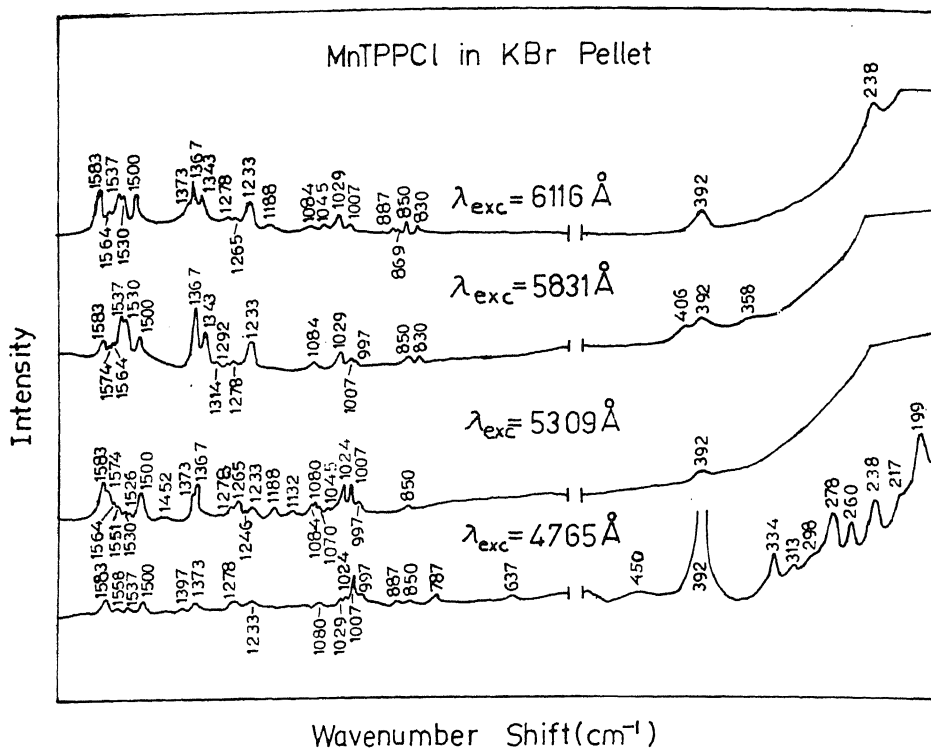


Figure 3a. Resonance Raman spectra of Mn(III)TPPCL in KBr pellets with different excitation wavelengths. The gap in the figure indicates a change of scale.

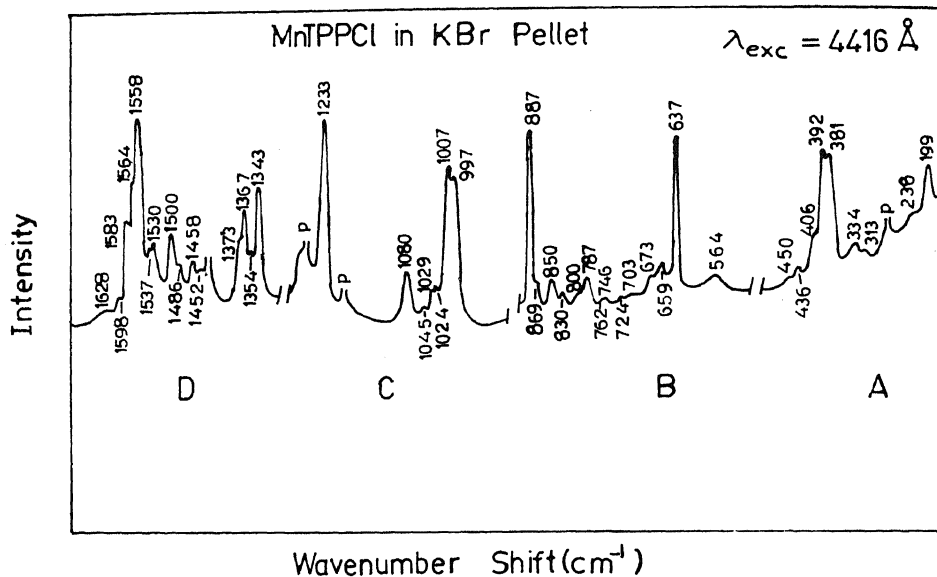


Figure 3b. Resonance Raman spectrum of Mn(III)TPPCL in KBr pellet with 4416 Å excitation wavelength. The breaks between different regions indicate difference in scale. The full scale counts rates for parts A, B, C and D are 2.5 k, 0.8 k, 1.5 k and 2.2 respectively. Plasma lines are indicated by 'p'.

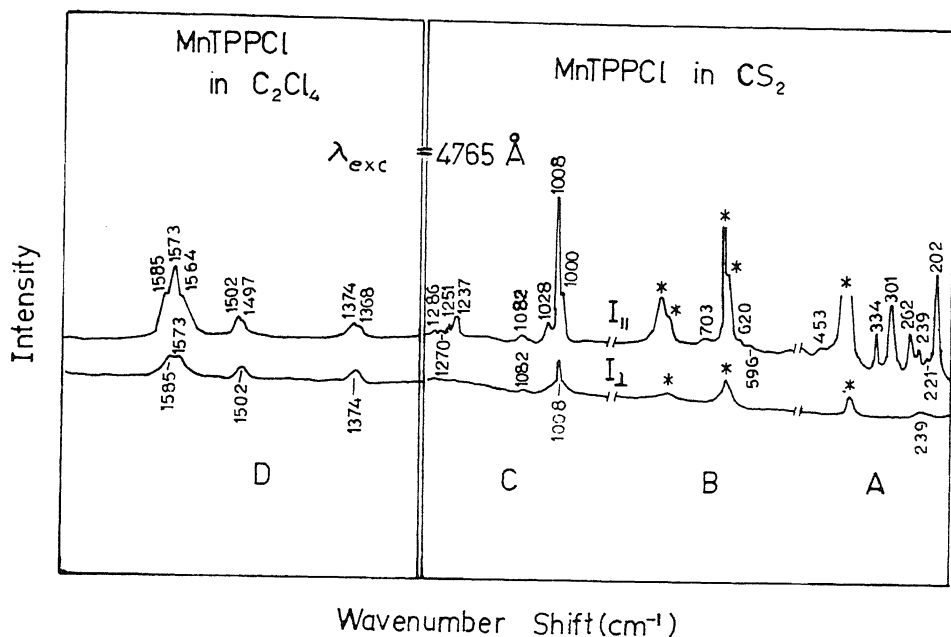


Figure 4a. Resonance Raman spectra of Mn(III)TPPCL in CS₂ (A–C) and C₂Cl₄ (D) solutions ($\sim 10^{-4}$ M concentration) with parallel (upper trace) and perpendicular (lower trace) components for $\lambda_{exc} = 4765$ Å. The breaks between different regions indicate difference in scale. The full scale count rates for part A for $I_{||}$ and $I_{\perp}$ are 1.2 k and 1.1 k respectively. Similarly, for parts B and C, they are 0.8 k, 0.7 k and 1.75 k, 1 k respectively. For part D, scales are same for $I_{||}$ and $I_{\perp}$ components. The solvent peaks and interfering bands by solvent are indicated by '*'.

Excitation in the 530 nm absorption enhances mainly higher frequency vibrations (figure 3a, table 2). One peculiar observation in this regard was that the sample seemed to be decomposed after a certain interval of time, in spite of the low power of the exciting radiation (~ 50 mW) and high speed of the spinning cell. Such degradation effects were not observed by excitation in any other absorption regions. Resonance Raman spectra of MnTPPCL in Py solution with excitation wavelength at 5309 Å have also been obtained and shown in figure 5b which has mainly the polarized bands. The RR spectra obtained by exciting in bands III and IV also show enhancement of mostly higher frequency modes. Several depolarized and anomalously polarized features also appear in addition to the polarized modes. On the other hand, RR spectra obtained by 4416 Å excitation show enhancement of both lower frequency and higher frequency vibrations.

3.2 Theoretical aspects of absorption spectra

The optical absorption spectra of normal metalloporphyrins can be interpreted in terms of the four orbital model (Gouterman 1961, 1973). Under D_{4h} symmetry, the highest occupied molecular orbitals are of $a_{1u}(\pi)$ and $a_{2u}(\pi)$ symmetry which are accidentally degenerate. The lowest empty molecular orbital is of $e_g(\pi^*)$ symmetry. The two transitions $a_{1u}(\pi) \rightarrow e_g(\pi^*)$ and $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ of E_u

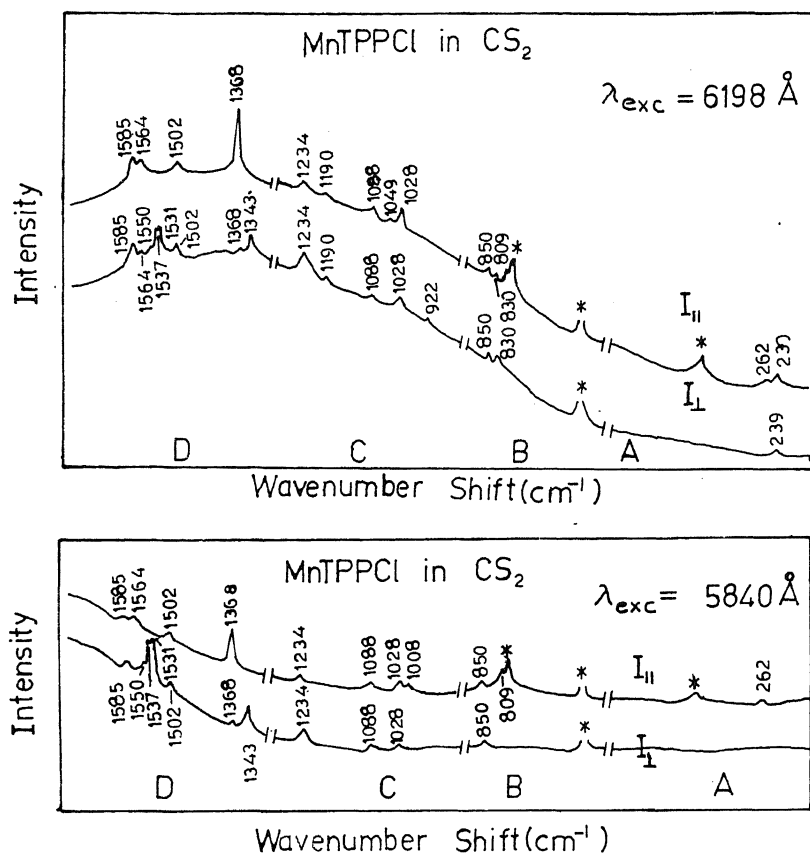


Figure 4b. Resonance Raman spectra of Mn(III)TPPCl in CS₂ solution ($\sim 10^{-4}$ M) with $\lambda_{exc} = 5840 \text{ \AA}$ (lower part) and $\lambda_{exc} = 6198 \text{ \AA}$ (upper part). The upper and lower traces in each part of the figure correspond to parallel and perpendicular components respectively. The breaks between different regions indicate difference in scales. For spectra with $\lambda_{exc} = 5840 \text{ \AA}$, the full scale count rates for part A for $I_{||}$ and $I_{\perp}$ are 4.1 k and 4 k respectively. Similarly, for parts B, C and D, they are 4.2 k, 4 k; 4.1 k, 4 k; and 5.5 k, 3 k respectively. For spectra with $\lambda_{exc} = 6198 \text{ \AA}$, the full scale count rates for part A for $I_{||}$ and $I_{\perp}$ are 3.1 k and 3 k, respectively. Similarly, for parts B, C and D, they are 6 k, 5.9 k; 7 k, 6 k and 6.1 k and 6 k respectively. The solvent peaks and bands which are interfered with by solvent are indicated by *.

symmetry are nearly degenerate and hence suffer configuration interaction producing an intense Soret band in which the transition dipole moments add and a weak α or $Q(0, 0)$ band in which the transition dipole moments largely cancel. β or $Q(1, 0)$ band arises due to vibronic interactions of the α and Soret bands and is related to the α band by, $\nu_{\beta}^{\max} = \nu_{\alpha}^{\max} + \nu_{\text{vib}}$.

Although the normal metalloporphyrin absorption spectra can be explained nicely by this model, the complexity of the Mn(III) porphyrin systems require much deeper understanding. As stated earlier, the disruption of the normal metalloporphyrin (π, π^*) spectra arises because of strong metal-porphyrin π -interactions. Theoretical calculations (Zerner and Gouterman 1966) predict that the metal d_{π} -orbitals for the manganese and iron match in energy with the

Table 2. Resonance Raman frequencies (cm^{-1}) of Mn(III)TPPCL in KBr pellets with different excitation wavelengths.

4416 Å	4765 Å	5309 Å	5831 Å	6116 Å
199 (<i>m</i>)	199 (<i>wm</i>)			
	217 (<i>w</i>)			
238 (<i>w, vbr</i>)	238 (<i>wm</i>)			238 (<i>wm</i>)
	260 (<i>wm</i>)			
	278 (<i>wm</i>)			
	298 (<i>vw</i>)			
313 (<i>vw</i>)	313 (<i>w</i>)			
334 (<i>w</i>)	334 (<i>wm</i>)			
			358 (<i>vw, br</i>)	
381 (<i>s</i>)				
392 (<i>s</i>)	392 (<i>vs</i>)	392 (<i>vw</i>)	392 (<i>w</i>)	392 (<i>wm</i>)
406 (<i>w, sh</i>)			406 (<i>w</i>)	
436 (<i>w</i>)				
450 (<i>vw</i>)	450 (<i>vw, br</i>)			
564 (<i>w</i>)				
637 (<i>m</i>)	637 (<i>wm</i>)			
659 (<i>w</i>)				
673 (<i>w</i>)				
703 (<i>vw</i>)				
724 (<i>vw</i>)				
746 (<i>vw</i>)				
762 (<i>vw</i>)				
787 (<i>w</i>)	787 (<i>wm</i>)			
800 (<i>vw, sh</i>)				
830 (<i>vw</i>)			830 (<i>w</i>)	830 (<i>wm</i>)
850 (<i>w</i>)	850 (<i>w</i>)	850 (<i>w</i>)	850 (<i>wm</i>)	850 (<i>wm</i>)
869 (<i>vw, sh</i>)				869 (<i>vw</i>)
887 (<i>m</i>)	887 (<i>w</i>)			887 (<i>w</i>)
997 (<i>m</i>)	997 (<i>wm</i>)	997 (<i>wm</i>)	997 (<i>vw</i>)	
1007 (<i>m</i>)	1007 (<i>s</i>)	1007 (<i>w</i>)	1007 (<i>w</i>)	1007 (<i>w</i>)
1024 (<i>w</i>)	1024 (<i>w</i>)	1024 (<i>m</i>)		
1029 (<i>w</i>)	1029 (<i>w</i>)		1029 (<i>m</i>)	1029 (<i>m</i>)
1045 (<i>vw</i>)		1045 (<i>vw</i>)		1045 (<i>w</i>)
		1070 (<i>w</i>)		
1080 (<i>wm</i>)	1080 (<i>vw</i>)	1080 (<i>wm</i>)		
		1084 (<i>w</i>)	1084 (<i>w, br</i>)	1084 (<i>w</i>)
		1132 (<i>w</i>)		
		1188 (<i>m</i>)		1188 (<i>w</i>)
1233 (<i>m</i>)	1233 (<i>wm</i>)	1233 (<i>wm, br</i>)	1233 (<i>ms, br</i>)	1233 (<i>ms, br</i>)
		1246 (<i>vw</i>)		
		1265 (<i>wm</i>)		1265 (<i>w</i>)
	1278 (<i>w, br</i>)	1278 (<i>w</i>)	1278 (<i>w</i>)	1278 (<i>w</i>)
			1292 (<i>w</i>)	
			1314 (<i>w</i>)	
1343 (<i>m</i>)			1343 (<i>ms</i>)	1343 (<i>m</i>)
1354 (<i>vw</i>)				
1367 (<i>m</i>)		1367 (<i>s</i>)	1367 (<i>s</i>)	1367 (<i>s</i>)
1373 (<i>wm, br</i>)	1373 (<i>wm</i>)	1373 (<i>m, sh</i>)		1373 (<i>sh</i>)
	1397 (<i>vw</i>)			
1452		1452 (<i>vw, br</i>)		
1458 (<i>wm</i>)				
1486 (<i>w, sh</i>)				

Table 2 (Contd.)

4416 Å	4765 Å	5309 Å	5831 Å	6116 Å
1500 (<i>m</i>)	1500 (<i>m</i>)	1500 (<i>m</i>) 1526 (<i>vw</i>)	1500 (<i>m</i>)	1500 (<i>m</i>)
1530 (<i>wm</i>)		1530 (<i>vw</i>)	1530 (<i>s</i>)	1530 (<i>m</i>)
1537 (<i>w</i>)	1537 (<i>vw</i>)	1551 (<i>vw</i>)	1537 (<i>s</i>)	1537 (<i>m</i>)
1558 (<i>s</i>)	1558 (<i>w, vbr</i>)			
1564		1564 (<i>w</i>) 1574 (<i>m, sh</i>)	1564 (<i>w</i>) 1574 (<i>w, sh</i>)	1564 (<i>wm</i>)
1583 (<i>m</i>)	1583 (<i>m</i>)	1583 (<i>s</i>)	1583 (<i>m</i>)	1583 (<i>s</i>)
1598 (<i>w</i>)				
1628 (<i>vw</i>)				

Abbreviations: v—very; w—weak; m—medium; s—strong; br—broad; sh—shoulder.

Table 3. Resonance Raman spectra of Mn(III)TPPCl in CS₂ solution ($\sim 10^{-4}$ M concentration).

4416 Å	4765 Å [†]	5840 Å	6198 Å	Assignment
	202 (<i>p</i>)			
	221 (<i>p</i>)			
	239 (<i>p</i>)		239 (<i>p</i>)	ν (Mn-N ₄)
	262 (<i>p</i>)	262 (<i>p</i>)	262 (<i>p</i>)	ν (Mn-Cl)
301 (<i>p</i>)	301 (<i>p</i>)			δ (Mn-N ₄)
334 (<i>p</i>)	334 (<i>p</i>)			
*396 (<i>p</i>)	*396	*396	*396	
	453			
	596			
	620			
	703			
	*787			
801				
809		809	809	
			830 (<i>ap</i>)	
		850 (<i>dp</i>)	850 (<i>dp</i>)	
887 (<i>p</i>)				
	1000 (<i>p</i>)		922	
	1008 (<i>p</i>)	1008 (<i>p</i>)		ν (C _{α} -C _{m})
	1028 (<i>p</i>)	1028 (<i>dp</i>)	1028 (<i>dp</i>)	
			1049	
	1082 (<i>p</i>)			δ (C _{β} -H)
		1088 (<i>dp</i>)	1088 (<i>dp</i>)	δ (C _{β} -H)
			1190 (<i>dp</i>)	
		1234 (<i>ap</i>)	1234 (<i>ap</i>)	ν (C _{α} -N) ₊
	1237 (<i>p</i>)			δ (C _{β} -H)
				ν (C _{m} -Ph),
				Phenylmode
	1251			
	1270			
	1286			
		1343 (<i>ap</i>)	1343 (<i>ap</i>)	

Table 3 (Contd.)

4416 Å	4765 Å [†]	5840 Å	6198 Å	Assignment
1368 (<i>p</i>)	1368 (<i>p</i>)	1368 (<i>p</i>)	1368 (<i>p</i>)	ν (C $_{\alpha}$ -N) ₊ δ (C $_{\beta}$ -H)
1374 (<i>dp</i>)	1374			
1452				ν (C $_{\alpha}$ -C $_{\beta}$) ₊
1458				δ (C $_{\beta}$ -H)
1497	1497			
1502	1502	1502 (<i>dp</i>)	1502 (<i>dp</i>)	ν (C $_{\beta}$ -C $_{\beta}$)
1526		1531 (<i>ap</i>)	1531 (<i>ap</i>)	
		1537 (<i>ap</i>)	1537 (<i>ap</i>)	ν (C $_{\alpha}$ -C $_m$)
		1550 (<i>sh</i>)	1550 (<i>sh</i>)	
1561				
	1564	1564	1564	
	1573			
1585	1585	1585	1585	

Abbreviations: *p* = polarized; *dp* = depolarized; *ap* = anomalously polarized; other abbreviations as in table 2.

The bands which are interfered with by the solvent peaks are indicated by **.

[†]The frequencies quoted from 1300–1700 cm⁻¹ region are in C₂Cl₄ solution.

porphyrin π -orbitals. Therefore strong mixing between the metal $e_g(d_\pi)$ levels and porphyrin π -levels can occur when they are energetically close. As a consequence, a number of additional bands become allowed and appear in the absorption. These bands were variously ascribed to porphyrin $\pi \rightarrow \pi^*$, charge-transfer or metal $d \rightarrow d$ transitions etc. In principle, each individual band is expected to show different solvent dependence, depending on its origin. For example, the bands arising due to metal d - d or charge-transfer transitions should be more sensitive to different solvents as compared to those arising from $\pi \rightarrow \pi^*$ transitions. However, experimentally this was not observed. The lack of observation of the expected solvent effects is also indicative of the complex electronic structure of the system. It is quite probable that the absorption peaks in the spectra do not arise due to a pure transition and may be an admixture of two or more transitions, so that the positions and intensities of the bands will vary in a complicated manner in different solvents. Therefore electronic absorption spectroscopy cannot provide a proper interpretation of the complicated absorption spectra of such systems. Resonance Raman studies can provide more useful information in such situations and we have been able to assign some of these bands using RR data in different spectral regions. We shall come back to this question after discussing the pertinent theoretical aspects of Resonance Raman scattering.

3.3 Theoretical aspects of resonance Raman scattering

When Raman spectra are excited in the region of an allowed electronic absorption, the vibrational modes which are expected to show enhancement are the ones which lend intensity to the electronic spectrum, i.e., they are vibronically active modes (Placzek 1934; Albrecht 1961; Behringer 1967; Tang and Albrecht 1970; Albrecht and Hutley 1971; Verma 1980). The intensity enhancement of specific vibrational

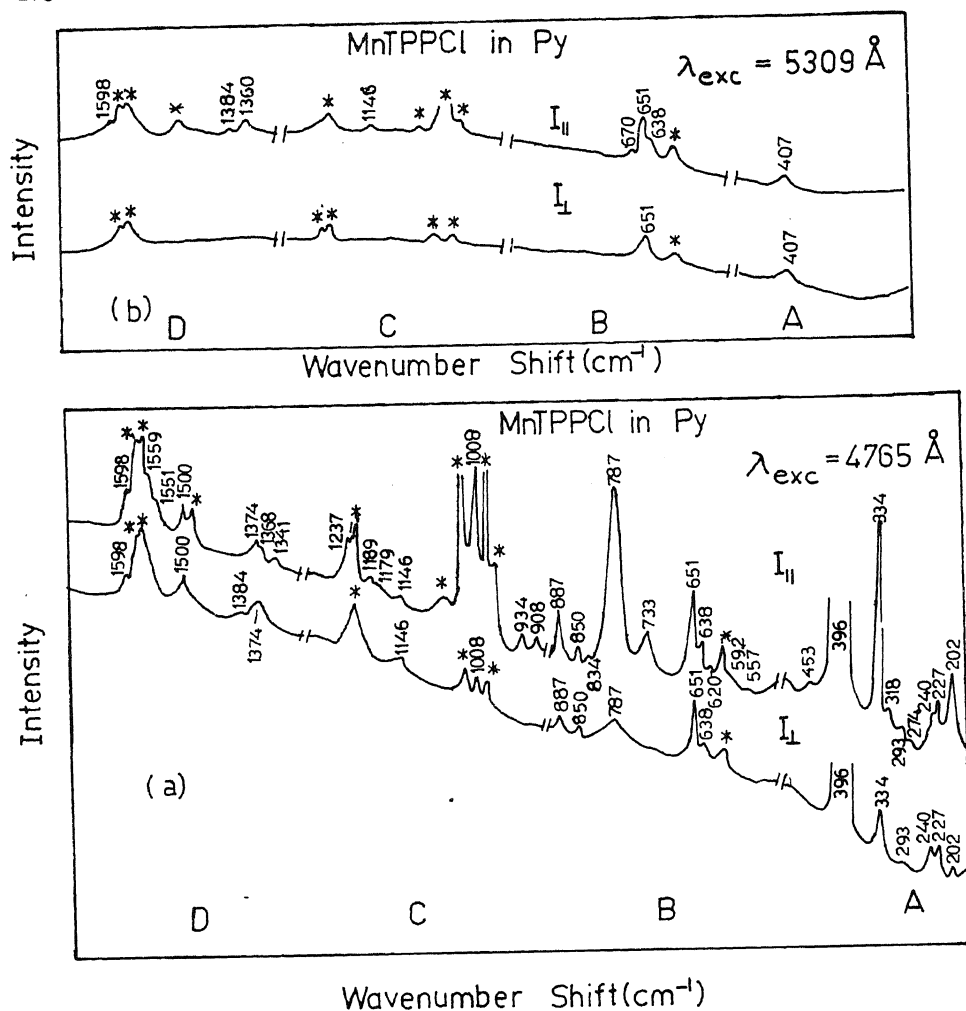


Figure 5. Resonance Raman spectra of Mn(III)TPPcI in pyridine ($\sim 10^{-4}$ M conc.) with $\lambda_{exc} = 4765 \text{ \AA}$ (lower part a) and $\lambda_{exc} = 5309 \text{ \AA}$ (upper part b) with parallel and perpendicular components. The breaks between different regions indicate difference in scales. For figure 5a, the full scale count rates for part A for $I_{||}$ and $I_{\perp}$ are 4.5 k and 2.5 k respectively. Similarly, for parts B, C and D, they are 2.2 k, 2 k; 4 k, 3 k and 4 k, 3.1 k, respectively. For figure 5b, the full scale count rates for part A for $I_{||}$ and $I_{\perp}$ are 2.55 k and 2.5 k respectively. Similarly, for parts B, C and D, they are 3.1 k, 3k; 5 k, 3.5 k and 6 k, 5 k respectively. The solvent peaks and bands which are interfered with by solvent are indicated by “*”.

modes under resonance excitation can take place through a mechanism involving either the A-type or the B-type term of the scattering tensor ($\alpha_{\rho\sigma}$), where

$$(\alpha_{\rho\sigma})_{ij} = (A_{\rho\sigma})_{ij} + (B_{\rho\sigma})_{ij} \quad (1)$$

ρ and σ being the molecular cartesian axes of the scattering tensor element $\alpha_{\rho\sigma}$. The A-term of the scattering tensor for the vibrational transition $i \rightarrow j$ is of the form (Albrecht and Hutley 1971)

$$(A_{jm})_e = \sum_{\alpha} \left[\frac{(M_{\sigma})_{ge} (M_p)_{eg}}{\nu_{\alpha,ge} - \nu_0 + i\Gamma_e} \right] \langle gi|ev \rangle \langle ev|gj \rangle \quad (2)$$

Here, $(M_{\sigma})_{ge}$ etc. stand for the matrix element $\langle g|R_{\sigma}|e \rangle$, R_{σ} , R_p are the dipole moment operators, $|gi\rangle$ and $|gj\rangle$ are vibrational states of the ground electronic state $|g\rangle$, $|ev\rangle$ is a vibrational state of the excited electronic state $|e\rangle$, Γ_e is related to the width of the excited electronic state $|e\rangle$. The B -type term of the scattering tensor for the vibrational transition $i \rightarrow j$ is of the form (Albrecht and Hutley 1971)

$$(B_{jm})_e = \frac{1}{h^2} \sum_{\alpha} \sum_{\beta} \sum_a \left[(M_{\sigma})_{ge} h_{\alpha}^{Q_a} (M_p)_{eg} \right. \\ \left. \langle gi|ev \rangle \langle ev|Q_a|gj \rangle + (M_p)_{ge} h_{\alpha}^{Q_a} (M_{\sigma})_{eg} \langle gi|ev \rangle \right. \\ \left. \langle ev|Q_a|gj \rangle \right] \frac{1}{(\nu_{\alpha,ge} - \nu_0 + i\Gamma_e)(\nu_{\beta} - \nu_e)}. \quad (3)$$

Here Q_a is the displacement of the a normal mode, $h_{\alpha}^{Q_a} = \langle e|\partial H/\partial Q_a|s\rangle$ and $(\partial H/\partial Q_a)$ is the change in the electronic Hamiltonian with the vibration of the ground state normal mode a .

The Raman activity associated with an A -type term involves separate resonances with individual zero-order electronic states and derives intensity from Franck-Condon overlap factors (2) arising from shifts in the equilibrium position and/or changes in the shape of the potential energy curve of the excited electronic state. The B -term is responsible for the Raman activity of those modes involved in vibronic mixing of two zero-order electronic states. The intensity of the modes which are enhanced via the B -term depends upon the product of the transition dipole moments of the electronic states being mixed (3), while the intensity of the modes enhanced via the A -term depends upon the square of the transition moment of the individual electronic state in resonance. This theoretical treatment can be applied to understand the absorption and RR spectra of Mn(III) porphyrin complexes. The ground state of Mn(III)-tetraphenyl porphyrin (TPP) can be written as follows (Asher and Sauer 1976)

$$|g\rangle = \phi_p \phi_m = NA \prod_i^m \left[\phi_{P_i}^2 \phi_{P_m}^{*2} d_{v_1}^1 d_{v_2}^1 d_{v_3}^1 d_{v_4}^0 d_{v_5-v_6}^0 \right]$$

The excited states of the system may be written as (Asher and Sauer 1976)

$$|e\rangle = N_e A \prod_i^{m-1} \left[\phi_{P_i}^2 \phi_{P_m}^1 \phi_{P_m}^1 d_{v_1}^1 d_{v_2}^1 d_{v_3}^1 d_{v_4}^1 d_{v_5-v_6}^0 \right],$$

$$|s\rangle = N_s A \prod_i^{m-2} \left[\phi_{P_i}^2 \phi_{P_{m-1}}^1 \phi_{P_m}^2 \phi_{P_m}^1 d_{v_1}^1 d_{v_2}^1 d_{v_3}^1 d_{v_4}^1 d_{v_5-v_6}^0 \right],$$

$$|d\rangle = N_d A \prod_i^m \left[\phi_{P_i}^2 \phi_{P_m}^{*2} d_{v_1}^1 d_{v_2}^0 d_{v_3}^1 d_{v_4}^1 d_{v_5-v_6}^1 \right]$$

$$\text{and } |c\rangle = N_c A \prod_i^{m-1} \left[\phi_{P_i}^2 \phi_{P_m}^1 \phi_{P_m}^{*2} d_{v_1}^1 d_{v_2}^1 d_{v_3}^2 d_{v_4}^1 d_{v_5-v_6}^0 \right],$$

where $|e\rangle$, $|s\rangle$ denote excited states reached by $\pi \rightarrow \pi^*$ transition, $|d\rangle$ denotes the excited state reached by $d \rightarrow d$ transition and $|c\rangle$ denotes the excited state reached by charge-transfer transition.

Here ψ_p , ψ_m represent the wavefunctions of TPP and metal respectively; N is the normalisation factor, A is the antisymmetrizer. ϕ_{p_i} are the occupied molecular orbitals in the ground state configuration of TPP, ϕ_p^* is the lowest unoccupied TPP molecular orbital and d_{xy} etc. represent the atomic orbitals of manganese. The superscripts indicate the electron occupancy of the orbitals.

The enhancement of resonance Raman features by the A -term will depend upon the factors $\langle gi|ev\rangle \langle ev|gj\rangle$. Within the limit of Born-Oppenheimer approximations, a molecular state can be separated into an electronic and vibrational components so that $\psi_e = \phi(q, Q)\chi(Q)$ where ϕ and χ are electronic and vibrational wavefunctions respectively and q, Q represent the electronic and nuclear coordinates. To proceed further, it is necessary to break $\chi(Q)$ in terms of modes mainly associated with the macrocycle and metal such that $\chi(Q) = \chi_p(Q)\chi_m(Q)$. Thus, $|gi\rangle = \phi_p \phi_m \chi_p^i \chi_m^i$ etc. For resonance with a state $|e\rangle$ reached by $\pi \rightarrow \pi^*$ excitation the Franck-Condon factors will be

$$\sum_v [\langle \chi_p^j | \chi_p^{ev} \rangle \langle \chi_p^{ev} | \chi_p^i \rangle] [\langle \chi_m^j | \chi_m^v \rangle \langle \chi_m^v | \chi_m^i \rangle],$$

Since the $\pi \rightarrow \pi^*$ transition involves charge redistribution in the porphyrin macrocycle, the distortion of the excited electronic state occurs within the macrocycle and as a result the macrocyclic modes are enhanced. Similarly, it can be shown that the change of the excited state configuration occurs within both the macrocycle and metal when the excitation occurs within a charge transfer band and as a result both metal and macrocyclic modes will be enhanced.

The vibronic mixing between two excited electronic states $|e\rangle$ and $|s\rangle$ occurs via the factors $\langle e|\partial H/\partial Q_a|s\rangle$. In order to see which type of vibrations would be enhanced by excitation in a particular absorption region, it is necessary to resolve the spatial properties of $\langle e|\partial H/\partial Q_a|s\rangle$. The operator $(\partial H/\partial Q_a)$ which mixes the electronic states is a one-electron operator, since the only part of the electronic Hamiltonian that depends on the nuclear position is the Coulomb potential between electrons and nuclei. The change of the electronic Hamiltonian with respect to the normal coordinate is given by

$$(\partial H/\partial Q_a) = -e' \sum_j \sum_n \partial(Z_n/r_{jn})/\partial Q_a,$$

where the summation is over all the electrons j and nuclei n , e' is the electronic charge, Z_n is the charge on the nucleus n , and r_{jn} is the distance between the electron j and nucleus n . For any one-electron operator we can write $o \equiv \int o(r)\phi'(r)dr$. Therefore $\langle e|O|s\rangle = \int \langle e|\phi'(r)|s\rangle O(r)dr$, where O is equivalent to $(\partial H/\partial Q_a)$ and $\langle e|\phi'(r)|s\rangle$ is known as the transition density. As has been shown by Albrecht (Albrecht 1961) that if two orbitals occupy different regions of the molecule, the contribution to Raman intensity by vibrational perturbation from the pair of orbitals will be very small or nonexistent.

Suppose now the two $\pi \rightarrow \pi^*$ excited states $|e\rangle$ and $|s\rangle$ are coupled by vibrational perturbation. Then we should have $\langle e|\phi'(r)|s\rangle = -e' \int \phi_{p_{m-1}} \delta(r-r_j) \phi_{p_m}^* dr_j$ where $\phi_{p_{m-1}}$ and ϕ_{p_m} are the highest energy occupied molecular orbitals. These orbitals are localized in the porphyrin macrocycle and

occupy similar regions. Therefore the vibrations which will show intensity enhancement via this term are those of the macrocycle. In a similar manner, it can be shown that (i) for coupling of a charge-transfer state, in which an electron goes to a d_{yz} or d_{xz} orbital of metal with a $\pi \rightarrow \pi^*$ excited state obtained from the same occupied molecular orbital, vibrations around the metal ion will be enhanced; (ii) for coupling of two different excited states formed by charge-transfer transitions which are obtained by excitation of electrons from the same porphyrin ground state molecular orbitals to the two different d -orbitals of metals, the vibrations related to metal-axial ligands may be picked out; and (iii) for coupling of two charge-transfer states which are obtained by excitation from different porphyrin π -orbitals to the same metal d -orbitals, vibrations related to the macrocycle should be enhanced. With this background, we shall try to probe the origin of different electronic absorption bands.

3.4 Assignment of the electronic absorption bands

The vibrations mostly enhanced by excitation in the absorption region of band V are related to the metal and therefore this band can be assigned to a charge-transfer transition. Excitations in absorption regions of the bands III and IV enhance many non-totally symmetric modes which are related to porphyrin macrocyclic vibrations. Similar features are observed in the Q -band excited RR spectra of metalloporphyrins with typical absorption spectra. Therefore bands III and IV can be correlated to α and β absorption band respectively. It is important to mention here that in addition to the metal related vibrations, band V excitation does reveal the presence of some macrocyclic modes and similarly in addition to the macrocyclic vibrations, band III excitation shows some metal-related modes. Although the enhancement of some macrocyclic vibrations in the charge-transfer excitation may occur via the A -term, both the A and B terms should contribute to the enhancement of macrocyclic vibrations when the excitation occurs in a $\pi \rightarrow \pi^*$ absorption. Therefore the enhancement of few low frequency vibrations, especially the Mn-Cl stretching mode vibrations, with α -band excitation indicates some charge-transfer character in the band III. It was proposed (Gouterman *et al* 1975; Gouterman 1978) that the charge transfer bands arising from electronic excitations $a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(d_\pi)$ of E_u symmetry mix with normal $\pi \rightarrow \pi^*$ transition of E_u symmetry, depending upon their relative energies. Our data is consistent with this model. We propose that the four electronic configurations of E_u symmetry obtained in this way mix via configuration interactions and give rise to the absorptions corresponding to bands III, V, V_a and VI. The relative intensity of all the bands will depend in a complicated way on the transition dipoles of the pure configurations and on the extent of mixing. However, band V has predominantly charge-transfer character and band III has mainly (π, π^*) character. We could not obtain RR data by exciting in the absorption regions of the bands V_a and VI which could be useful in further confirmation of the above assignment scheme. The enhancement of both the lower and higher frequency vibrations with $\lambda_{ex} = 4416 \text{ \AA}$ can be understood in the following way. The absorption in this region will have contributions from bands V, V_a and VI and since these bands have mixed character of charge transfer and (π, π^*) transitions, this may be responsible for enhancement of Raman lines corresponding to both the metal related modes and the macrocyclic modes.

The number of Raman bands observed in the KBr pellet is generally large compared to the spectra obtained in solution. It is known that the molecules occupy lower site symmetry and are distorted in the solid form. Therefore more bands will be expected in the RR spectra with KBr pellets than in solution due to site and correlation field splittings and Raman activity of the forbidden IR modes.

The reversal of intensity of bands III and IV in Py solution is probably related to the change in porphyrin π -levels. The axial positions are occupied by the Py molecules in Py solution which indicates that the out-of-plane distance of the metal with respect to the porphyrin plane should be different in Py solution from that in MnTPPCl in CS₂. RR data obtained with $\lambda_{\text{ex}} = 4765 \text{ \AA}$ supports this view. The change in the metal-nitrogen ligand strength should affect the $a_{2u}(\pi)$ level of the molecule, since it has electron density through the pyrrole nitrogens. As the intensity of the α -band depends considerably on the relative energy gap between the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals it is expected that this will influence the intensity of the α -band considerably. Finally, the absorption at $\sim 425 \text{ nm}$ in Py solution which disappears in other solvents can be tentatively correlated with metal-pyridine charge-transfer transition. Similar features were observed in (TPP)Fe(II)Py₂ (Kobayashi and Yanagawa 1972) as well as in [(OEP)M(Py)₂] systems where M=Fe(II), Ru(II), OS(II) (Schick and Bocian 1984). However, further work will obviously be helpful in confirming this assignment.

The most interesting results were obtained from RR spectra by excitation in the 530 nm absorption region. The RR bands observed correspond mainly to macrocyclic vibrations. The appearance of mainly the macrocyclic vibrations via the *A*-term can occur provided this absorption originates from a $\pi \rightarrow \pi^*$ transition. Enhancement of mainly macrocyclic vibrations can also occur via the *B*-term in the case where the two coupled states both originate from $\pi \rightarrow \pi^*$ transition or when the two states that are coupled are reached by two charge-transfer transitions which originate from different porphyrin π -levels but end in the same metal-*d* level. However, the modes which should be expected to be enhanced mainly via the *B*-term are non-totally symmetric. On the other hand, polarization data in Py solution indicates that mainly the totally symmetric vibrations are enhanced by excitation with 5309 Å laser line. Even the Raman bands obtained in pellet spectra correspond mainly to the totally symmetric modes as observed in solution. This implies that the enhancement of vibrations with excitation in the 530 nm absorption occurs via the *A*-term and hence should be of $\pi \rightarrow \pi^*$ origin. In view of the present evidence, one of the plausible assignments for this band may be singlet $\rightarrow$ triplet (π, π^*) transition. This transition is spin-forbidden and not observed in the normal absorption spectra. The mixing of $e_g(\pi^*)$ and $e_g(d_\pi)$ levels can cause extra features in the absorption and can also introduce large spin-orbit coupling providing a relaxation pathway for the singlet triplet transition to occur. Kobayashi *et al* (1973) have shown that in Mn(III) and Fe(III) porphyrin systems, the charge-transfer states not only mix with the singlet (π, π^*) absorption, but also with the triplet (π, π^*) absorption, making singlet $\rightarrow$ triplet (π, π^*) transition mixed with some charge-transfer character, partly allowed. However, the bands in the near IR region have been mainly attributed to singlet $\rightarrow$ triplet (π, π^*) origin. It was shown previously (Gouterman 1978) that the porphyrin lowest triplet states are of (π, π^*) origin and should be represented as a pure single configuration arising from either $(a_{1u} \rightarrow e_g)^T$ or $(a_{2u} \rightarrow e_g)^T$ transitions because the coupling integral which

causes mixing of the singlet transitions vanishes for the triplet states if the molecule has D_{4h} symmetry. However, in Mn(III) porphyrin systems the interactions between the central metal and porphyrin ligand cause large perturbations in the electronic structure and as a result, the above formulation may breakdown resulting in similar configuration interaction even in the excited triplet states. We propose that the band at ~ 530 nm and one of the bands in the near IR region arise due to singlet-triplet (π, π^*) transitions. The decomposition of the samples by excitation with the 5309 Å laser lines may be understood qualitatively in terms of the longer lifetime of the triplet state. The molecules in the excited triplet state may undergo photo-decomposition before they return to the ground state. Therefore, the present observation also seems to support the assignment of this band of singlet $\rightarrow$ triplet (π, π^*) origin. Thus, although a reasonable explanation for the band around 530 nm can be offered, a proper understanding will require detailed theoretical study.

3.5 Activation of the phenyl modes

Earlier workers (Burke *et al* 1978; Schick and Bocian 1983; Kozuka and Iwaizumi 1983; Hofmann and Bocian 1984) have reported the presence of some phenyl modes in the RR spectra of FeTPP systems. This implies that phenyl groups are conjugated with the whole macrocycle and also that the internal modes of the phenyl groups must be coupled to the electronic transitions of the whole macrocycle. In the ground state, the phenyl rings are twisted almost perpendicularly with the macrocycle and therefore conjugation between the phenyl rings and the macrocycle cannot occur. The conjugation of the phenyl rings and observations of the phenyl modes in the RR spectra were attributed to an excited state interaction (Burke *et al* 1978). It was suggested that during the Q -state excitation the electron density moves towards the meso-carbon atoms, which provide a driving force for rotation of the phenyl groups in the porphyrin plane resulting in electron delocalization through the phenyl groups. The bands at $996\text{ cm}^{-1}(p)$, $1030\text{ cm}^{-1}(p)$, and at $1598\text{ cm}^{-1}(p)$ in FeTPP systems and at $1640\text{ cm}^{-1}(p)$ and $1240\text{ cm}^{-1}(p)$ in CoTPP systems were associated with the phenyl vibrations based on the meso carbon deuteration shift. Following the argument of Burke *et al* (1978) the phenyl modes are expected to be more strongly enhanced by excitation in band III as well as by excitation in the ~ 530 nm absorption region. In the RR spectra of Mn(III)TPPCL, the feature at 997 cm^{-1} is more strongly enhanced with $\lambda_{\text{ex}} = 4416\text{ Å}$, 4765 Å , 5309 Å , less strongly with $\lambda_{\text{ex}} = 5831\text{ Å}$ and not observed with $\lambda_{\text{ex}} = 6116\text{ Å}$ in the KBr pellet spectra. The observation of the band with $\lambda_{\text{ex}} = 5309\text{ Å}$ is in agreement with the previous suggestion, while non-observation of this band with excitation in the α -band region does not support this contention. On the other hand, the band at 1598 cm^{-1} is not detectable with 5309 Å excitation, but was observed with 4416 Å and 6282 Å excitations. Although the appearance of this band during α -band excitation does support its assignment to phenyl group vibration, its absence with the 5309 Å excitation contradicts this proposal. Another band at 1030 cm^{-1} has also been assigned to a phenyl mode. In MnTPPCL, two bands are seen in this region in the pellet spectra. Owing to very small frequency difference, these two features mostly overlap and one of them may be hidden under the envelop of the other in the solution spectra. However, our observation of only

one medium intense and depolarized band in this region in the solution spectra with visible band excitation does not support its assignment to a phenyl group mode. We have observed a polarized band at 1237 cm^{-1} in CS_2 with $4765\text{ \AA}$ excitation while it was not detectable with other excitations in solution. Bands at similar positions were also observed in RR spectra of non-phenyl metalloporphyrins (Verma and Bernstein 1974; Mendelsohn *et al* 1975; Asher and Sauer 1976). Thus our study does not provide distinct evidence of conjugation of the phenyl groups with the macrocycle either in the ground or in the excited electronic states of the system. Even the RR study of meso-formyl and meso-nitro substituted Ni(II) octaethyl porphyrin (Ivanova and Berdyugin 1984) does not support the idea of conjugation between the meso-substituents and porphyrin π -system. Therefore the features at 997 , 1030 , 1240 and 1598 cm^{-1} may be related to kinematically perturbed porphyrin macrocyclic modes.

3.6 Dispersion of depolarization ratio (ρ_I)

Under resonance scattering, the polarizability tensor $\alpha_{\rho\sigma}$ need not remain symmetric (Placzek 1934) and the modified expression for linear depolarization ratio is given as

$$\rho_I = \frac{I_{\perp}}{I_{\parallel}} = \frac{3\gamma_s^2 + 5\gamma_{as}^2}{45\bar{\alpha}^2 + 4\gamma_s^2},$$

where $\bar{\alpha}$, γ_s and γ_{as} represent the isotropic, symmetric anisotropic and antisymmetric anisotropic polarizability tensor invariants, respectively.

The possible range of ρ_I values for vibrations of different symmetry species under various point groups can be used to determine the symmetry of the system (McClain 1971). Since the manganese atom is out of the porphyrin plane, the symmetry of the system is expected to be C_{4v} for symmetric placement of the phenyl groups. As has been shown by McClain (1971) that under the point group D_{4h} or (C_{4v}), the range of ρ_I values expected for the A_{1g} (A_1 in C_{4v}), A_{2g} (A_2 in C_{4v}), B_{1g} (B_1 in C_{4v}) or B_{2g} (B_2 in C_{4v}) type of vibrations are $\frac{1}{8}-\frac{3}{4}$, ∞ and $\frac{3}{4}$ respectively. The depolarized and anomalously polarized modes should not show any dispersion. Similar results are expected for the D_{2d} and D_4 point group symmetries. However, two well-resolved bands at 850 cm^{-1} (dp) and at 1012 cm^{-1} (ap) show slight dispersion. ρ_I varies between 0.6 and 0.75 for the 850 cm^{-1} band and between 2 and 3 for the 1012 cm^{-1} band with different excitations. This indicates that the structure of the chromophore is distorted from C_{4v} symmetry. One of the plausible explanations for such distortion may be given in terms of the possible orientations of the phenyl groups. X-ray structural data of *bis*-(imidazole)- $\alpha, \beta, \gamma, \delta$ -tetraphenylporphyrinato Fe(III)Cl (Collins *et al* 1972) indicates that in these systems, the dihedral angle made by the phenyl rings with the porphyrin plane in the adjacent 1 and 4 positions (figure 1) is 88° and that made by the phenyl rings of the other two adjacent positions with the molecular plane is 76° . In that case the molecular symmetry of MnTPPCl is C_s . It is probable that even in solution the molecular symmetry of MnTPPCl molecule as a whole is C_s because of similar orientation of the phenyl groups. This lowering of symmetry can give rise to enhancement of additional bands as compared to the C_{4v} structure.

4. Conclusion

We can summarize the findings as follows: The intense band V can be interpreted as arising due to charge-transfer transitions while bands III and IV are mainly of $\pi \rightarrow \pi^*$ origin. The absorption at ~ 530 nm may be due to singlet-triplet (π, π^*) transitions. No direct evidence for the enhancement of the phenyl modes was found; therefore conjugation of the phenyl rings with the porphyrin macrocycle is less likely although the system is highly complicated and more studies may be required to decide this point. Moreover, the variation of depolarization ratio for some bands with exciting frequency indicates that the effective molecular symmetry of the chromophore is lowered from C_{4v} , and the rigorous molecular symmetry may be only C_s .

Acknowledgements

Financial support from the Department of Science and Technology, New Delhi, and from the Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged.

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Binding of ketoprofen with bovine serum albumin

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MS received 23 February 1987; revised 15 June 1987

Abstract. The binding of Ketoprofen, i.e. 2-(3-benzoylphenyl) propionic acid, with bovine serum albumin, BSA, was investigated by equilibrium dialysis. Limiting the studies to low drug (10 to 100 μM) concentrations, the binding data correspond to a single set of binding sites, namely, the high-affinity sites. Scatchard and Klotz methods of analysis have been employed to determine the binding parameters for the high-affinity sites. The binding constant does not vary significantly with [BSA] in the concentration range 7.25 to 21.5 μM . The molar ratio, [drug]/[protein] is found to be a critical factor in determining the nature and number of binding sites. The quenching of intrinsic fluorescence of the protein at the emission wavelength of 346 nm indicates the presence of tryptophan in the binding site.

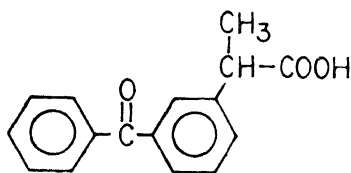
Keywords. Ketoprofen; bovine serum albumin; binding constant; high-affinity sites.

1. Introduction

Serum albumin is a very interesting receptor macromolecule in the study of drug-receptor interactions. It has a number of relatively specific binding sites for drugs and endogeneous compounds and is characterized by the presence of several binding regions (Krag-Hansen 1983). Two specific sites for acidic drugs have been characterized in serum albumin (Sudlow *et al* 1975, 1976; Birkett *et al* 1980); they are known as the azopropazone/warfarin site and the diazepam/benzodiazepine site in terms of the drugs or groups having specific binding affinity for the sites. Drugs which bind to the diazepam site are aromatic carboxylic acids largely ionized at physiological pH. The configuration of these molecules is extended and the negative charge is located at one end of the molecule away from the nonpolar region.

In the present work, we have investigated the interaction of 2-(3-benzoylphenyl)-propionic acid with bovine serum albumin, BSA. The substrate is a new non-steroidal anti-inflammatory drug having the pharmaceutical name, Ketoprofen. The interaction of Ketoprofen with BSA as the receptor would be of interest to gain insight into the pharmacodynamics and toxicology of the drug which is useful for arthritis and related conditions (Fowler *et al* 1980). 2-(3-benzoylphenyl)-propionic acid or Ketoprofen belongs to the class of aryl propionic acid drugs which selectively bind to the diazepam site. The drug-macromolecule interaction has been examined employing equilibrium dialysis and fluorescence quenching.

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2-(3-benzoylphenyl)propionic acid or Ketoprofen

2. Experimental

Bovine serum albumin fraction V (Loba Chemie Co., India), a defatted sample and Ketoprofen (The Pharmaceutical Company of India, Ltd.) were used without further purification. Dialysis membranes (Sigma Chemical Co., USA) were subjected to washing in hot water for about two hours before use. The experiments were carried out at pH = 7.1 using an $\text{Na}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ mixture of 0.1 M concentration. The concentration of BSA is expressed on the basis of its molecular weight (69,000). [BSA] ranging from 7.25 μM to 21.5 μM have been used in the present study. The initial concentration of the drug (C_0) is varied from 10 μM to 300 μM .

Equilibrium dialysis experiments were carried out as described in the literature (Rosenberg and Klotz 1960). Dialysis experiments were performed at 30°C for 48 hours. Experiments were carried out in the absence of BSA and the binding of the drug onto the dialysis membrane was found to be negligible. Equilibrium concentrations of the drug, C , were found out from the measurements of absorbance in the uv region at 261 nm using a Carl-Zeiss Specord UV-VIS spectrophotometer. Blanks were obtained from control experiments carried out under the same conditions in the absence of the drug. The concentration of the bound drug (C_B), and hence, the molar ratio of bound drug to BSA ($r = C_B/[\text{BSA}]$) have been obtained from these to calculate the binding parameters. To evaluate the binding constant for the high-affinity sites, observations were restricted to $[\text{drug}] = 10 \mu\text{M}$ to 100 μM .

Fluorescence measurements have been made with an Aminco Bowman spectrophotofluorometer. Fluorescence-quenching titrations were carried out by addition of Ketoprofen to a known concentration of BSA. [Ketoprofen] = 6 to 150 μM , and [BSA] = 7.25 μM and 21.5 μM , have been employed for fluorescence studies. The protein fluorescence spectrum due to tryptophan was obtained using an excitation wavelength of 280 nm. The maximum fluorescence values at the emission wavelength of 346 nm were measured as a function of [Ketoprofen]. Correction for quenching due to bulk-absorption or self-absorption (Velick *et al* 1960) has been applied and the actual quenching curve corresponds to corrected fluorescence values.

3. Results and discussion

The binding of a substrate to several classes of sites on a protein molecule is represented by the Scatchard equation (Scatchard 1949) in terms of the molar ratio of the bound substrate to protein r , as

$$r = \sum_i \frac{n_i K_i C}{1 + K_i C}, \quad (1)$$

where $n_i K_i$ is the binding constant corresponding to the i th class of sites with intrinsic binding constant K_i and number of binding sites n_i and C is the equilibrium or free concentration of the substrate. Inspection of (1) reveals that a plot of r/C versus r would be a curve if there are more than one class of binding sites, and the analysis of data of BSA-Ketoprofen system proved to be so in the C_0 range 10 μM to 300 μM . It has been evident that the data corresponding to low values of r , i.e., $r < 4$ may be regarded as belonging to one set of binding sites, namely, the high-affinity sites. Considering only this single set of binding sites, (1) is transformed into the Klotz equation (Klotz *et al* 1946) or the Scatchard equation.

$$\frac{1}{r} = \frac{1}{n_1} + \frac{1}{n_1 K_1 C}, \quad \text{Klotz equation}, \quad (2)$$

$$\frac{r}{C} = n_1 K_1 - r K_1, \quad \text{Scatchard equation}. \quad (3)$$

We have evaluated the binding constant $n_1 K_1$, the number of binding sites n_1 and the intrinsic binding constant K_1 for the high-affinity sites making use of (2) and (3). The other set of binding sites, termed the low-affinity sites, is not subjected to any detailed analysis to determine $n_2 K_2$ since the error involved in these values would be greater.

The multiplicity of binding sites, evident when the [drug] is varied widely from 10 to 300 μM , is no longer observed when [drug] is limited to $< 100 \mu\text{M}$ corresponding to $r < 4$. Table 1 shows the data obtained for $[\text{BSA}] = 21.5 \mu\text{M}$. Figure 1 shows the above data analyzed in terms of the Klotz equation and figure 2 in terms of the Scatchard equation. Analysis of the data by the method of least squares yields $n_1 K_1$ and n_1 and the binding parameters (table 2) by both Klotz and Scatchard methods are in good agreement. The binding constants do not change significantly with $[\text{BSA}]$. The mean value of the intrinsic binding constant is found to be $(1.24 \pm 0.33) \times 10^5 \text{ M}^{-1}$ (table 2). The number of binding sites is found to be $n_1 \approx 5$ at $[\text{BSA}] = 7.25 \mu\text{M}$ and $n_1 \approx 4$ at $[\text{BSA}] = 21.5 \mu\text{M}$. Considering the uncertainty associated with n_1 (table 2), the two values of n_1 do not differ significantly. However, a probable explanation for the difference in the value of n_1

Table 1. Binding of Ketoprofen to BSA in 0.1 M phosphate buffer.
[BSA] = 21.5 μM ; temperature = 30°C; pH = 7.1

C_0 (μM)	C (μM)	r	(1/ r)	(r/C) $\times 10^{-4}$ (M^{-1})	(1/ C) $\times 10^{-4}$ (M^{-1})
40.00	12.30	2.57	0.389	20.89	8.10
50.00	19.00	2.88	0.347	15.15	5.26
60.00	25.80	3.18	0.314	12.32	3.87
70.00	34.40	3.31	0.302	9.62	2.90
80.00	44.10	3.33	0.300	7.55	2.26
90.00	52.00	3.53	0.283	6.78	1.92

C_0 = Initial concentration of the drug; C = equilibrium concentration of the drug;
 r = molar ratio of bound drug to albumin.

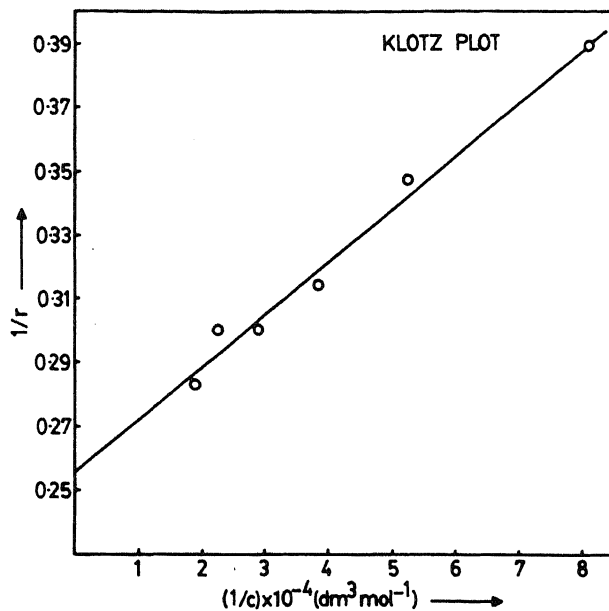


Figure 1. Klotz plot for the BSA-Ketoprofen system corresponding to the high-affinity binding sites. $[\text{BSA}] = 21.5 \mu\text{M}$, $[\text{Ketoprofen}] = 10$ to $100 \mu\text{M}$, $\text{pH} = 7.1$ and 30°C .

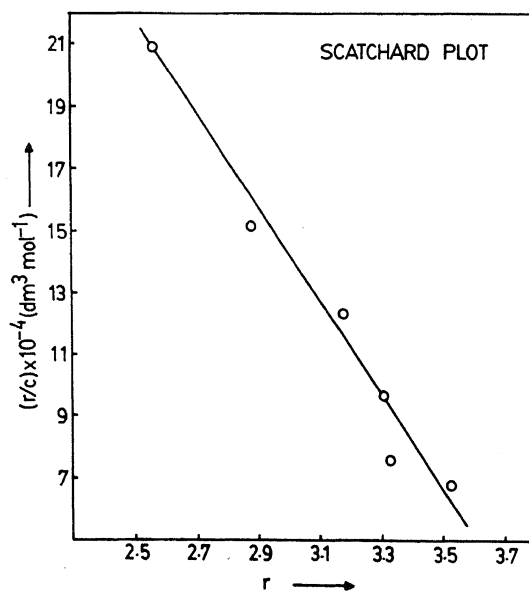


Figure 2. Scatchard plot for the evaluation of binding parameters relating to the high-affinity binding sites. $[\text{BSA}] = 21.5 \mu\text{M}$, $[\text{Ketoprofen}] = 10$ to $100 \mu\text{M}$, $\text{pH} = 7.1$ and 30°C .

Table 2. Binding parameters for the BSA-Ketoprofen system.Temperature = 30°C; pH = 7.1; [Buffer] = 0.1 M; [Drug] = 10 to 100 μ M.

Method of analysis	[BSA] (μ M)	$n_1 K_1 \times 10^{-5}$ (M^{-1})	n_1	$K_1 \times 10^{-5}$ (M^{-1})	Mean value $K_1 \times 10^{-5}$ (M^{-1})
Klotz method	7.25	6.24(± 0.87)	4.80(± 0.14)	1.30	1.24 ± 0.33
Scatchard method	7.25	4.83(± 0.36)	5.26(± 0.63)	0.92	
Klotz method	21.50	6.09(± 0.30)	3.89(± 0.02)	1.57	
Scatchard method	21.50	6.13(± 0.03)	3.90(± 0.31)	1.57	

The values given in parenthesis are standard deviations.

would be the following. Since the initial concentration of the drug, C_0 , is the same at both 7.25 μ M and 21.5 μ M of BSA, the relative concentrations of the drug to BSA, $C_0/[BSA]$ would be three times more at low [BSA] than at high [BSA]. This would have led to the utilization of the fifth binding site in the protein molecule which is otherwise inactive at low $C_0/[BSA]$ ratio. In other words, the molar ratio of substrate to protein also appears to determine the number of active binding sites in the macromolecule.

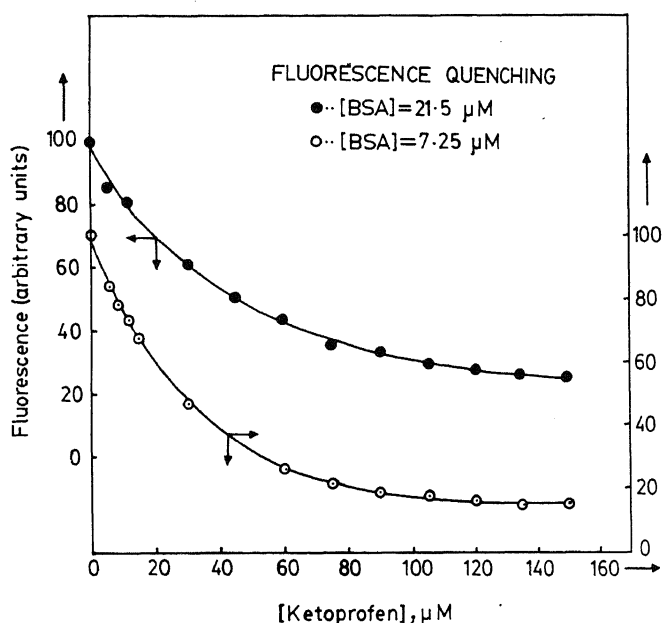
The low-affinity sites are involved in binding only at high values of r , namely, $4 < r < 8$ and at [drug] = 100 to 300 μ M. It is evident from this that the relative ratio $C_0/[BSA]$ and hence $C_B/[BSA]$, i.e., r are important in determining the nature of binding sites. The second set of binding sites would have been left unnoticed if the study has not been performed at high $C_0/[BSA]$. The binding constant, $n_2 K_2$, for the low-affinity sites is found to be of the order of 10^4 .

Ketoprofen is an aryl propionic acid drug. Since the carboxylic acid group would exist in the form of the anion at the experimental pH, the anion is expected to interact electrostatically with cationic amino acids of the type lysine, arginine and histidine. In addition to this, the non-polar part of the drug would interact with the hydrophobic aryl residues of albumin. Recent studies (Wanwimolruk *et al* 1983) show that aryl propionic acid non-steroidal anti-inflammatory drugs and medium chain fatty acids (C_8 to C_{10}) bind strongly to the diazepam site, which is a hydrophobic cleft about 16 Å deep and about 8 Å wide in the albumin molecule with a cationic group located near the surface. The molecular size as well as the presence of both anionic and hydrophobic groups in Ketoprofen suggest the diazepam site as the probable binding site for Ketoprofen.

The intrinsic binding constant for BSA-Ketoprofen system is about five times smaller than that for the related system involving human serum albumin, HSA-F 1594 (Urien *et al* 1984) as evident from table 3. In the case of Ketoprofen, the carbonyl group is in between the two aryl groups and this reduces the interaction of the aryl residues with the hydrophobic residues of albumin. The position of carbonyl group is not so unfavourable in the case of F 1594. For the interaction of Flurbiprofen, Ibuprofen and Naproxen with HSA immobilized in microparticles (Kober and Sjoeholm 1980), the binding constants are of the order of 10^6 (table 3). The absence of the hydrophilic carbonyl group in the above drugs explains the higher binding constants relative to Ketoprofen since hydrophilic groups such as hydroxyl and carbonyl have been shown to reduce the binding affinity of such aryl propionic acid drugs (Urien *et al* 1984).

Table 3. Comparison of the binding constants for BSA-Ketoprofen and related systems.

Substrate	Pharmaceutical name	$K_1 \times 10^6$ (M^{-1})	Reference
2-(3-benzoylphenyl)propionic acid	Ketoprofen	0.12	This work
2-methyl-3-(4-phenylcarboxy-phenyl)propionic acid	F 1594	0.54	Urien <i>et al</i> (1984)
2-(6-methoxy-2-naphthyl)-propionic acid	Naproxan	1.8	Kober and Sjöeholm (1980)
2-(4-isobutylphenyl)propionic acid	Ibuprofen	1.3	Kober and Sjöeholm (1980)
2-(2-fluoro-4-biphenyl)-propionic acid	Flurbiprofen	5.0	Kober and Sjöeholm (1980)

**Figure 3.** The quenching of fluorescence of BSA as a function of [Ketoprofen]. [Ketoprofen] = 6 to 150 μ M, pH = 7.1 and 30°C. BSA concentration: (●) 21.5 μ M; (○) 7.25 μ M.

For BSA-Ketoprofen system, fluorescence quenching studies have also been made to gain insight into the nature of the binding site. BSA contains two tryptophan residues that emit fluorescence with maximum at 346 nm by excitation at 280 nm. This intrinsic tryptophanyl fluorescence of the protein can be utilized to monitor drug-protein interactions (Teale and Weber 1957). The absence of quenching of fluorescence does not imply the absence of drug-protein interaction whereas the quenching of protein fluorescence by the drug can be taken to indicate drug-protein interaction, in the absence of any conformational change in the protein favouring quenching.

A progressive decrease in the intensity of the intrinsic protein fluorescence has been observed with increase in the concentration of Ketoprofen (figure 3). The maximum quenching at saturation reaches 80–90%. As the drug exhibits no absorbance at $\lambda > 300$ nm, there is no appreciable overlap of the emission spectrum of the protein and the absorption band of Ketoprofen. Hence it is not likely that the quenching phenomenon is due to nonradiative energy transfer. Quenching has its origin at the source of fluorescence emission, namely, in the direct perturbation of the fluorophore. In other words, the drug comes in direct proximity with the tryptophan residue. This implies that tryptophan is a part of the binding site in the interaction of Ketoprofen with BSA and also leads to the conclusion that hydrophobic forces are involved in binding.

Acknowledgement

The authors acknowledge the CSIR, New Delhi, for financial support and the Pharmaceutical Company of India Ltd., for the gift sample of Ketoprofen.

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A new method of determining solubility of salts and simple salt mixtures at higher temperatures (0 to 200°C) and up to 100 bars pressure

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MS received 13 October 1986; revised 13 July 1987

Abstract. A new apparatus has been designed and fabricated to determine the solubility of salts and simple salt mixtures at higher temperatures and pressures. The apparatus can be used to determine the solubility of salts at temperatures from 0 to 200°C and pressures upto 100 bars. The apparatus has been tested by determining the solubility of NaCl at temperatures from 30 to 200°C, while that of KCl was determined from 30 to 200°C. The phase equilibrium of the ternary system NaCl–KCl–H₂O has been established at two different temperatures 129.2°C and 159.2°C and under pressures upto 50 bars; extrapolations were upto 200°C.

Keywords. Solubility; hydrothermal fluids; brines; power plant; invariant point.

1. Introduction

Knowledge about the solubilities of salts in water is important in understanding the existence and nature of these salts occurring in the earth as minerals or as hydrothermal fluids, to understand sub-oceanic hydrothermal springs and also to have an idea about the separation of such salts from a mixture of them. Such knowledge about the solubilities of salts at their saturation equilibrium also throws light on the thermodynamic stability of salt deposits (Marshall 1985) on the disposal of radioactive wastes in ocean (Clyne *et al* 1981), and on the scale formations of salts in boiler feed water and in power plants (Tomlinson 1985).

A large amount of experimental data is available in the literature on the solubility of several salts at higher and normal temperatures and normal pressures. The solubilities of salts at higher temperatures as well as higher pressures are also of equal importance as for instance the pressure inside the earth varies from one bar to about thousands of bars and temperature varies from the normal to a few thousands of degrees. However, very few such data are available in the literature, particularly for mixtures.

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The solubilities of salts at higher temperatures, approximately 400°C, is usually determined by three different methods, namely, quenching methods, visual observation and indirect methods (Marshall 1985; Cytne *et al* 1981; Booth and Bidwell 1950; Valyashko 1973). However, all these methods have their own drawbacks (Marshall 1985; Valyashko 1973).

Therefore in the present study we have designed and constructed a new apparatus using which the solubilities of salts at higher temperatures (upto 200°C) and at pressures (upto 100 bars) can be determined. The same apparatus can also be used to study the solubilities of simple ternary systems like NaCl – KCl – H₂O in which no double-salt formation occurs.

2. Apparatus

The autoclave along with the sample collector unit is shown in figure 1a. The autoclave Z, made of stainless steel (1880 CrNi), and is of 90 mm length, its inside and outside diameters are 40 mm and 50 mm respectively. The inside of the cell is lined with Ti metal (2 mm in thickness) so as to reduce the corrosion of the cell due to highly concentrated salt solutions.

The lid of the cell is a temperature-resistant stainless steel flange (material ATS 340). To minimize pressure leakages a teflon ring is used together with two delta rings between the cell and the lid as shown in figure 1b. In order to take out samples for analysis from the system the lid is provided with a capillary K of 67.5 mm length and 3 mm inner diameter. One end of the capillary which is inside the solution is equipped with three small meshes one on another, each of which is less than 0.1 mm. With the help of a spindel press SP (figure 1a) samples are drawn from the system without altering the equilibrium conditions. The lid is also provided with a stirrer R of length 79 mm and diameter 17 mm as shown in figure 1b. Furthermore, the lid consists of a pressure transducer part P, which in turn is connected to a millivoltmeter (standardised against the Bourdon pressure gauge).

The temperature of the experimental solution is measured with the help of a chromel-alumel thermoelement T₃ immersed in the solution. Two more such thermoelements T₁ and T₂ are used to record the temperatures of the bottom and middle parts of the autoclave. The temperatures at the valves, capillaries, and spindel press are controlled by similar thermoelements T₄, T₅ and T₆ respectively. The sample collector PG is made of titanium and has a volume of 13 cm³.

Initially N₂ gas at 15 bars pressure is applied through valves V₃ and V₄. The autoclave is placed in an aluminium jacket A1 which is heated by a heating coil H₁. The valves and capillaries are heated by H₂ and another heating coil H₃ is used to heat the spindel press.

3. Experiments

For binary systems experiments were carried out by taking a saturated solution (at room temperature) of the respective salt and N₂ then adding excess of the salt into the solution in the autoclave. The autoclave was closed and N₂ gas at 15 bars pressure initially applied. The system was continuously stirred while heating slowly to the

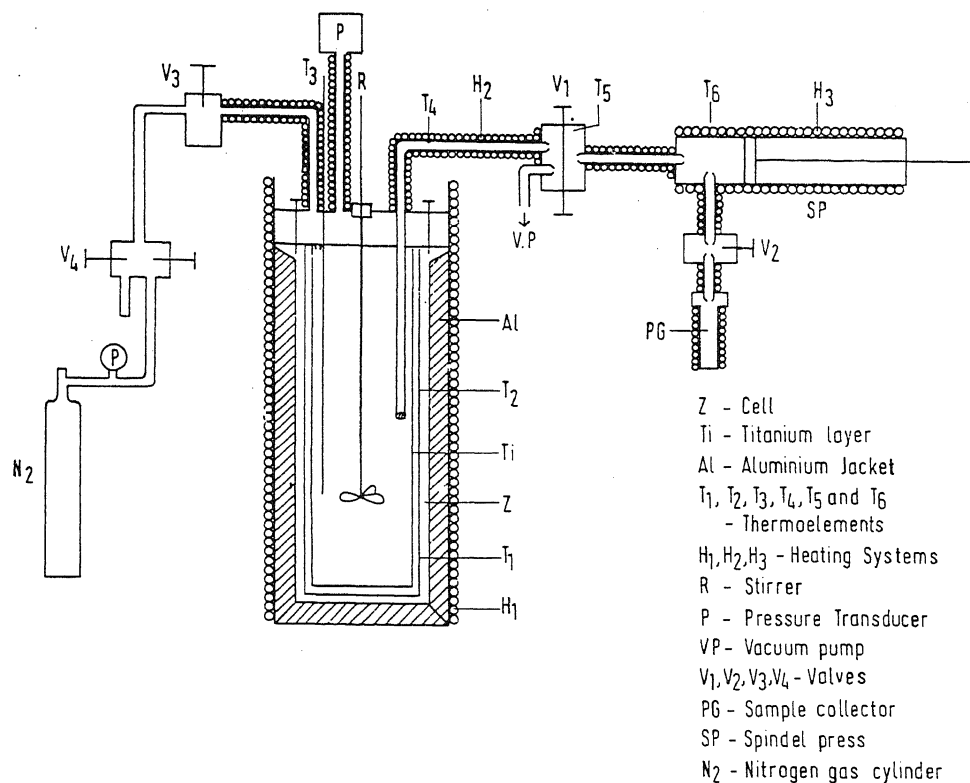


Figure 1a. Apparatus for determining the solubility of aqueous salt systems at higher temperatures and pressures.

desired temperature. The system was maintained at the required temperature ($\pm 0.2^\circ\text{C}$) for about 3 to 4 hours to attain equilibrium. Before taking out the sample the stirring of the solution was stopped and the pressure was noted. The sample was drawn into the collector using the spindel press without disturbing the equilibrium of the system. The sample was cooled along with the system, weighed and analysed for its composition. Merck extra-pure grade KCl and Merck GR grade NaCl were used without further purifications. N₂ gas 99.99% purity, supplied by Griesheim, was used. Chloride was estimated by titration and potassium by atomic absorption spectroscopy. All experiments were repeated till reproducible results were obtained. For ternary systems the experiments were carried out in a similar fashion by adding small amounts of the second salt. This was continued till the invariant point was reached, where both the salts are in equilibrium with their saturated solution. The point was checked by starting the experiments from both A and B points.

4. Results and discussion

4.1 Binary system

Experiments were carried out to determine the solubilities of individual salts NaCl and KCl at temperatures 30°C to 200°C under pressure. The data (± 0.05) are given

Table 1. Solubility of NaCl in water at 16 bars.

Temperature (°C)	Concentration of solution, g % (by weight)
30.0	26.42
75.6	26.72
100.4	27.98
123.1	28.17
149.5	29.62
200.0	34.19

Table 2. Solubility of KCl in water at 16 bars.

Temperature (°C)	Concentration of solution, (g % by weight.)
30.0	26.32
75.2	33.45
100.5	36.21
112.5	37.66
123.7	38.31
145.2	39.42
153.4	39.69
168.5	41.91
195.2	44.08

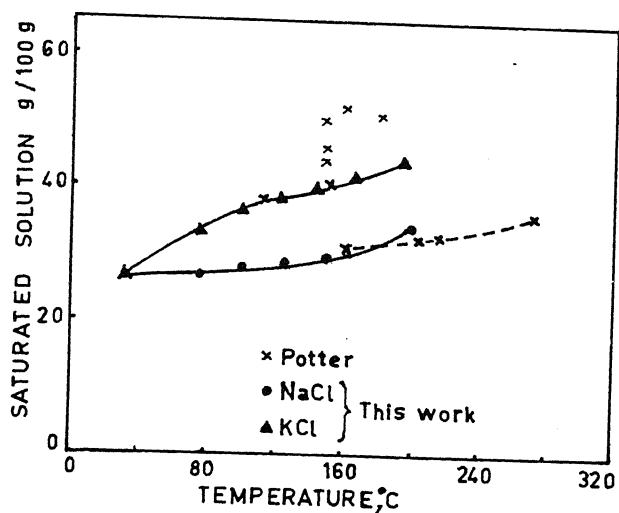
**Figure 2.** Temperature effect on the solubility of NaCl-H₂O and KCl-H₂O (Ctyne *et al* 1981).

Table 3. Solubility data in ternary system NaCl-KCl-H₂O.

Temperature, °C	Point	Concentration of the solution*		Solid phase
		NaCl	KCl	
25°C	A	26.48	0.0	NaCl
		24.58	3.34	NaCl
		22.11	8.16	NaCl
	I	20.42	11.14	NaCl + KCl
		13.45	15.71	KCl
		12.32	16.58	KCl
	B	—	26.52	KCl
129.2°C	A	29.50	—	NaCl
		28.72	3.59	NaCl
		27.74	6.84	NaCl
		25.16	7.52	NaCl
		23.59	9.52	NaCl
		22.16	13.87	NaCl
	I	17.70	25.57	NaCl + KCl
		12.32	26.08	KCl
		13.49	28.88	KCl
		6.34	32.51	KCl
		0.76	37.21	KCl
	B	—	38.61	KCl
159.2°C	A	31.18	—	NaCl
		27.16	6.52	NaCl
		27.63	11.50	NaCl
		25.84	10.29	NaCl
		19.74	20.93	NaCl
		22.05	22.11	NaCl
	I	16.07	29.49	NaCl + KCl
		15.87	26.62	KCl
		10.21	32.31	KCl
		4.72	36.62	KCl
	B	—	40.37	KCl

*In g/100 g saturated solution 25°C data is from Siedel and Linke (1965).

with data for 25°C from the literature (Siedel and Linke 1965). These data are plotted in figures 3 and 4 as triangular and prismatic projections respectively showing the extrapolation of the ternary system from 159.2°C to 200°C by dashed lines. One can see from figure 3 that the solubilities of individual salts increase as the temperature increases. The increase in solubility of KCl is much more pronounced than that of NaCl, in accordance with the observations made using binary systems. The effect of temperature is more pronounced on the solubility of KCl and particularly on the invariant point I, as seen from figures 3 and 4. The curves AI and IB show the boundary surfaces between the solid salt and solutions. One can clearly see the effect of temperature on the fields occupied by individual salts NaCl and KCl and the shift in the invariant point in the triangular and prismatic projections of the system. The present method is useful only for simple salts and salt mixtures (with no double-salt formation).

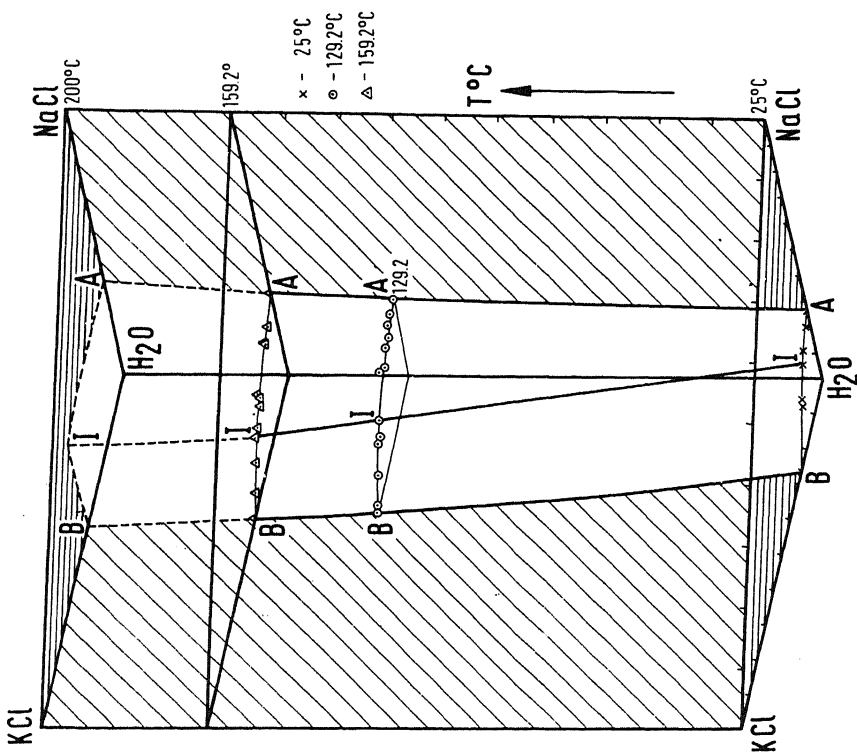


Figure 4. Prismatic projections of NaCl-KCl-H₂O showing the isotherms at 25, 129.2 and 159.2°C.

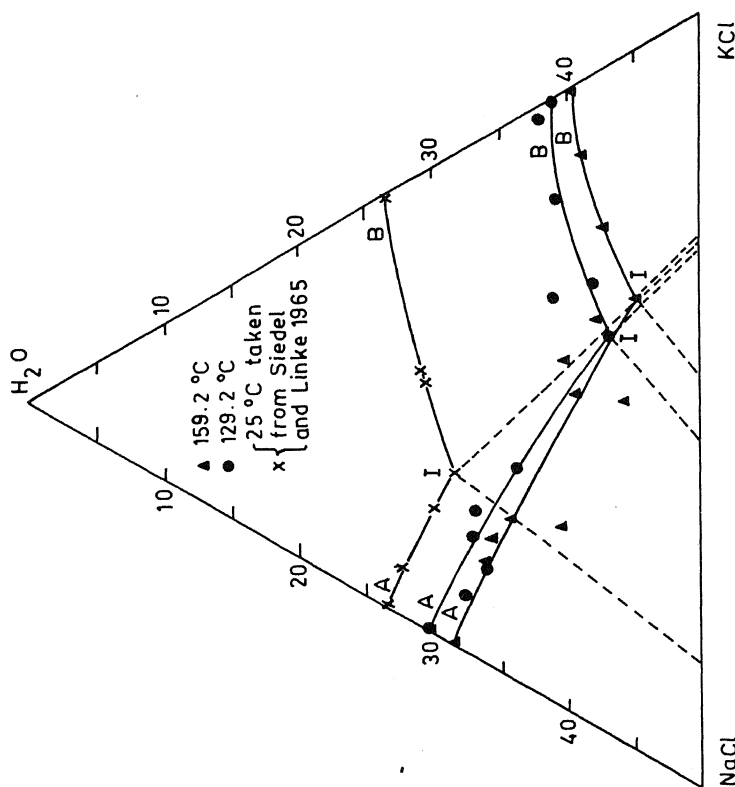


Figure 3. Solubility isotherms in the system NaCl-KCl-H₂O.

Acknowledgements

One of the authors, V R K S Susarla, thanks DAAD for the fellowship and also Petrographic Department, University of Karlsruhe, for permission to carry atomic absorption measurements.

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Studies on binary and ternary complexes of Co(II) and Ni(II) ions

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MS received 25 July 1986; revised 20 May 1987

Abstract. Potentiometric investigations on the binary and ternary complexes of the type MA, MB and MAB have been carried out, where $M(II) = Co(II)$ and $Ni(II)$; A = iminodiacetic acid (IMDA) and B = oxydiacetic acid (ODAA). The formation constants and free energies of formation for binary and ternary complexes have been reported.

Keywords. Iminodiacetic acid; oxydiacetic acid; formation constant; free energy of formation.

1. Introduction

Binary complexes of iminodiacetic acid (IMDA) and oxydiacetic acid (ODAA) with various metals have been extensively investigated by Chaberek and Martell (1952), Misumi and Aihara (1966), Liberty and Napoli (1971), Napoli (1972), Klein and Kersels (1964), Ramamoorthy and Santapa (1969), Miyazaki and Toei (1975). Mixed ligand complexes of various metals with IMDA are widely studied (Kuglar and Carey 1970; Ramamoorthy and Santapa 1971; Joshi and Bhattacharya 1980; Katkar and Munshi 1985). However, literature survey further reveals that mixed ligand complexes of Co(II) and Ni(II) with IMDA as primary ligand and ODAA as secondary ligand have not been studied so far. In view of this it was, therefore, considered of interest to study the formation constants of the following systems:

Co(II) and Ni(II)-IMDA (1:1 complexes), Co(II) and Ni(II)-ODAA (1:1 complexes), Co(II) and Ni(II)-IMDA-ODAA (1:1:1 complexes).

2. Experimental

2.1 Materials

The chemicals used were of BDA (AR) grade. Solutions of $CoSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$ were prepared in conductivity water and stock solutions were standardized by known methods. Solutions of the ligands IMDA (A) ODAA (B) were prepared by direct weighing. Perchloric acid (0.025 M) was prepared from stock solution and the solution was standardized against standard sodium hydroxide solution.

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2.2 Apparatus

The pH titrations were carried out at $25 \pm 0.5^\circ\text{C}$ (maintained thermostatically) with the help of Philips pH-meter (PR 9405 M). The instrument was calibrated using buffer tablets of pH 4.0 and 9.2.

2.3 Conditions of study

The experiments were performed in a specially designed double-walled beaker of capacity 250 ml made of pyrex glass. The total volume of the solution (50 ml), ionic strength ($\mu = 0.10 \text{ M NaClO}_4$) and concentration of metal ions and ligand ($5 \times 10^{-4} \text{ M}$) were kept constant at the beginning of the titration. All the titrations were performed in duplicate in order to establish the reproducibility of the measurements. The following sets of solutions were prepared and titrated against alkali (0.25 M):

(i) *Acid and ligand*

(a) $2.5 \times 10^{-3} \text{ M HClO}_4$

(b) $2.5 \times 10^{-3} \text{ M HClO}_4 + 5 \times 10^{-4} \text{ M IMDA/ODAA}$

(ii) *1:1 Binary system*

(c) $b + 5 \times 10^{-4} \text{ M metal ion}$

(iii) *1:1:1 Ternary system*

(d) $a + 5 \times 10^{-4} \text{ M IMDA} + 5 \times 10^{-4} \text{ M ODAA} + 5 \times 10^{-4} \text{ M metal ion}$

2.4 Calculations

The pK_1 and pK_2 values determined by the method of Irving and Rossotti (1953) for the acids agree well with the literature values. The values were further refined by computational techniques (Irving and Rossotti 1953; Dubey and Mehrotra 1967): (i) the interpolation at half $\bar{n}$ values, (ii) the pointwise method, (iii) the curve fitting method, and (iv) the correction term method. The formation constants $\log K_{MA}$, $\log K_{MB}$ and $\log K_{MAB}$ of the binary and ternary systems were calculated by the method of Ramamoorthy and Santapa (1970, 1971). The following expressions were utilized for calculations:

$$K_{MA} = \frac{T_M - [A] \cdot X}{[A]^2 \cdot X},$$

$$K_{MAB} = \frac{T_M - \left\{ \frac{1}{2} [A] \cdot X \right\}}{\left(\frac{1}{2} \right)^3 \cdot A^3 \cdot X},$$

where T_M , A and X have their usual meanings. These calculations were carried out with the help of ECIL TDC 316 Computer using FORTRAN IV and COBOL languages in the various programs. Free energies of formations were determined using the following expressions:

$$\Delta F^0 = -2.303 RT \log K_{MA} / \log K_{MB} / \log K_{MAB}$$

for binary and ternary complexes (table 1).

Table 1. Formation constants and free energy of formation of the complexes.

System	Stoichiometry	pH range investigated	log K	$-\Delta F^0$ (kcal mole ⁻¹)
Co(II)-IMDA	1:1	5.20–6.58	7.08 ± 0.04 (6.95) ^a	9.659 ± 0.055
Ni(II)-IMDA	1:1	3.50–5.25	8.35 ± 0.17 (8.21) ^a	11.392 ± 0.232
Co(II)-ODAA	1:1	3.85–4.23	3.24 ± 0.35	4.420 ± 0.477
Ni(II)-ODAA	1:1	4.20–5.55	3.32 ± 0.21	4.529 ± 0.286
Co(II)-IMDA-ODAA	1:1:1	3.65–4.20	6.69 ± 0.22	9.127 ± 0.300
Ni(II)-IMDA-ODAA	1:1:1	3.80–4.20	7.73 ± 0.01	10.546 ± 0.014

^a Literature value: Chaberek and Martell (1952)

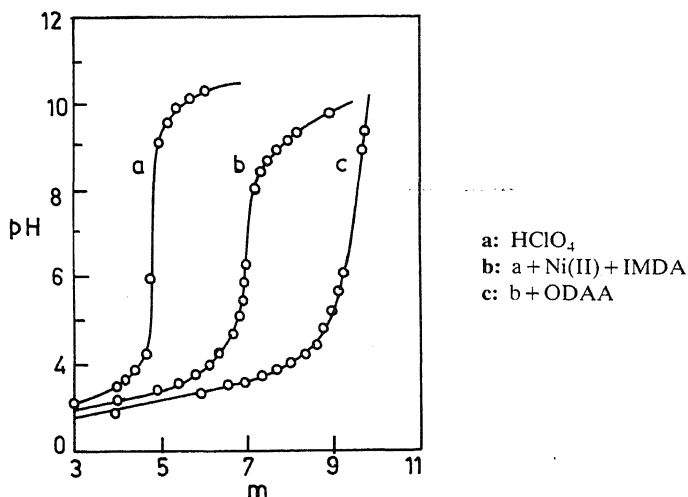
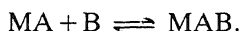
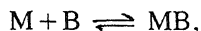
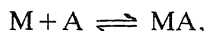


Figure 1.

3. Results and discussion

The potentiometric curves of both the metals involved were found to be very similar in nature. Therefore, the curves of different systems for only one metal, viz. Ni(II)-IMDA and Ni(II)-IMDA-ODAA systems, are shown (i.e. b and c respectively) in figure 1 for the sake of brevity. Curve a represents the acid titration curve. For curve a, $m \approx 5.0$, therefore, for curve b, the inflection is assumed to take place at $m \approx 2$ [$\approx 7.0 - 5.0$] which indicates the formation of the 1:1 complex in Ni(II)-IMDA system (m being the number of moles of base added per mole of the metal ion or ligand). The 1:1:1 ternary complex system, Ni(II)-IMDA-ODAA, is represented by curve c, the inflection of which takes place at $m \approx 4$ [$\approx 9.0 - 5.0$]. It may be attributed to the stepwise addition of ligands to the metal ion resulting in the formation of 1:1:1 ternary complex.

The equilibria for M(II)-binary and M(II)-ternary systems can be represented by the following equations:



The formation of heteroligand-metal-complexes in these systems is further evidenced by (i) lowering in pH in comparison with the binary versus ternary systems, (ii) non-appearance of solid phase during the titration.

The stability constant values of all the systems are given in table 1. A perusal of these indicates that the values of $\log K_{MAB}$ (Ni(II)/Co(II)-IMDA-ODAA) are lower than those of $\log K_{MA}$ (Ni(II)/Co(II)-IMDA) systems. Lowering in the stability of ternary complexes in comparison to binary complexes has also been reported by other workers (Limaye and Saxena 1985).

Acknowledgements

The authors are grateful to Prof S N Sawhney for encouragement. One of them (JKN) thanks the Kurukshetra University authorities for a fellowship.

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Erratum

'On scattering from fractal lattices' by Harjinder Singh and P K Chattaraj, *Proc. Indian Acad. Sci. (Chem. Sci.)* **99**, pp. 47–51 (1987).

Equation (2) should read as

$$\psi_{\mathbf{k}}^{+\text{d}_f}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \int G_+(\mathbf{r}, \mathbf{r}') V^{\text{d}_f}(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}') \, \text{d}\mathbf{r}', \quad (2)$$



Catalytic decomposition of hydrogen peroxide on fine particle ferrites and cobaltites

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MS received 10 April 1987; revised 23 June 1987

Abstract. The kinetics of heterogeneous decomposition of hydrogen peroxide on fine particle ferrites, MFe_2O_4 and cobaltites, MCo_2O_4 , where $M = Mn, Fe, Co, Ni, Zn$ and Mg , have been investigated. The decomposition of H_2O_2 was found to be first order at low concentration (0.3%) and zero order at high concentration (30%) of H_2O_2 . The catalytic activity of cobaltites on the decomposition of H_2O_2 is found to be better than ferrites. The observed catalytic behaviour of ferrites and cobaltites has been attributed to their fine particle nature, large surface area and electronic structure.

Keywords. Hydrogen peroxide decomposition kinetics; ferrites; cobaltites.

1. Introduction

The kinetics of decomposition of hydrogen peroxide has been studied by a large number of workers (Schumb *et al* 1955). The interest in the kinetics of H_2O_2 decomposition stems from its use in oxygen production, power generation and electrolytic reduction of oxygen in which H_2O_2 is an intermediate. The choice of a suitable catalyst for the decomposition of H_2O_2 has proved to be difficult due to the high cost of catalysts like silver oxide, platinum and palladium black as well as the poor reactivity of cheap catalysts like MnO_2 , Co_2O_3 , Fe_2O_3 etc. Recently, Onuchukwu (1984), Goldstein and Tseung (1974) and Cota *et al* (1964) have reported that ferrites; cobalt-iron oxide spinels ($Co_xFe_{3-x}O_4$, $x = 0-3$) in particular, show high activity in the decomposition of H_2O_2 . The catalytic activity of these oxides has been attributed to their electronic structure, composition, surface morphology and microstructure (surface area).

It is rather surprising that although Co-Fe oxide spinels have been investigated in great detail there is only one report (Tarasevich and Efremov 1980) on the use of cobaltites, MCo_2O_4 , where $M = Mn, Co, Ni$ and Mg , as catalysts for the decomposition of H_2O_2 . It has been observed that $NiCo_2O_4$ dispersed over carbon black exhibits maximum activity for H_2O_2 decomposition and catalytic activity is attributed to the increased dispersedness of cobaltites on carbon black. Therefore, it was considered interesting to study the heterogeneous decomposition of H_2O_2 in the presence of fine particle ferrites, MFe_2O_4 , and cobaltites, MCo_2O_4 , where

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M = Mn, Fe, Co, Ni, Zn and Mg. The choice of these catalysts is warranted by the fact that they have large surface areas ($12\text{--}140\text{ m}^2/\text{g}$) and are prepared by the low temperature decomposition of novel hydrazine precursors $\text{N}_2\text{H}_5\text{M}_{1/3}\text{M}'_{2/3}(\text{N}_2\text{H}_3\text{COO})_3\text{H}_2\text{O}$, M = Mn, Fe, Co, Ni, Zn and Mg; M' = Fe or Co. The novelty of the precursors is their autocatalytic combustion behaviour, with the evolution of large amounts of gases, leaving behind fine particle oxides (Ravindranathan and Patil 1987; Ravindranathan *et al* 1987).

2. Experimental

2.1 Preparation of the oxides

The preparation and characterisation of hydrazine precursors to fine particle ferrites, $\text{N}_2\text{H}_5\text{M}_{1/3}\text{Fe}_{2/3}(\text{N}_2\text{H}_3\text{COO})_3\text{H}_2\text{O}$ (Ravindranathan and Patil 1987) and cobaltites $\text{N}_2\text{H}_5\text{M}_{1/3}\text{Co}_{2/3}(\text{N}_2\text{H}_3\text{COO})_3\text{H}_2\text{O}$ (Ravindranathan *et al* 1987), where M = Mn, Fe, Co, Ni, Zn and Mg, have already been described. Only the preparation of fine particle ferrites and cobaltites is described here.

Ferrites: The precursors $\text{N}_2\text{H}_5\text{M}_{1/3}\text{Fe}_{2/3}(\text{N}_2\text{H}_3\text{COO})_3\text{H}_2\text{O}$ were ignited in a silica crucible and allowed to decompose autocatalytically in the absence of a flame or an external heat source. The crystals decompose with the evolution of NH_3 , H_2O , N_2 , H_2 , and CO_2 . The decomposition products, ferrites (MFe_2O_4), are fine, voluminous residues.

Cobaltites: The precursors $\text{N}_2\text{H}_5\text{M}_{1/3}\text{Co}_{2/3}(\text{N}_2\text{H}_3\text{COO})_3\text{H}_2\text{O}$ were ignited in a silica crucible and allowed to decompose autocatalytically as described above. The decomposition products, cobaltites (MCo_2O_4), were also fine in nature.

Some important properties like XRD data, particle size, BET surface area (determined by N_2 adsorption at liquid nitrogen temperature) of ferrites and cobaltites have been summarised in table 1.

Table 1. Some properties of fine particle ferrites and cobaltites.

Compound	XRD data				
	a^* (nm)	Crystallite size (nm)	Particle density (g/cm^3)	Particle size (micron)	Surface area (m^2/g)
MgFe_2O_4	0.8388	13	4.118	3.15	114
MnFe_2O_4	0.8321	6	3.269	1.65	140
CoFe_2O_4	0.8418	10	3.649	2.5	116
NiFe_2O_4	0.8359	22	3.574	3.2	26
ZnFe_2O_4	0.8477	9	3.437	3.4	108
MgCo_2O_4	0.8130	10	3.0517	2.20	47
MnCo_2O_4	0.8113	24	5.46	0.82	24
FeCo_2O_4	0.8222	6.5	3.919	4.35	116
NiCo_2O_4	0.8118	10	5.7	—	12.4
ZnCo_2O_4	0.8172	14	5.06	4.56	65

* Powder diffraction file, Inorganic vol. PDIS-10iRB, Joint Committee on Diffraction standards, Pennsylvania; 1967.

2.2 Kinetics of H_2O_2 decomposition

Stabiliser free H_2O_2 (AnalaR BDH, 30% w/v) solution was used in all the experiments. The solution was standardised by standard KMnO_4 before the run. The kinetics of H_2O_2 decomposition was studied using 30% and 0.3% solutions. Precautions were taken to protect the solutions from light and heat during storage.

A schematic diagram of the experimental set-up used is shown in figure 1. This is a slightly modified version of the gasometric method (Deren *et al* 1963). The catalyst is taken in the reaction vessel which is immersed in a thermostat. To the side limb of the reaction vessel is attached a 'V' shaped tube, well-protected from light, containing the H_2O_2 solution. The reaction rate is deduced in terms of the volume of oxygen evolved in the liquid phase. The oxygen evolved is measured with the help of the manometer filled with water coloured with potassium dichromate. As oxygen is collected in the manometer, the water level in the right arm lowers while it rises in the left. In a given interval of time the difference in water levels in the arms of the manometer, which is proportional to the amount of O_2 evolved, can be determined by running down water from the burettes at the left. The large burette of 50 ml capacity is used to drain off larger volumes while the smaller 10 ml capacity is used to make minor corrections.

In a typical experiment, a few milligrams of the catalyst were placed in the reaction vessel and attached to the set-up. About 10 ml of the H_2O_2 solution were poured into the 'V' tube, which was attached to the reaction vessel. The reaction vessel and the 'V' tube were immersed in thermostat maintained at $30^\circ\text{C} \pm 0.5^\circ\text{C}$ and atmospheric pressure. The whole set-up was left undisturbed till the reaction vessel and the tube attained thermal equilibrium. During this time, O_2 evolved due to self-decomposition of H_2O_2 , was adjusted by bringing the manometric liquid to the initial level before the start of the run. After equilibrium the H_2O_2 solution was

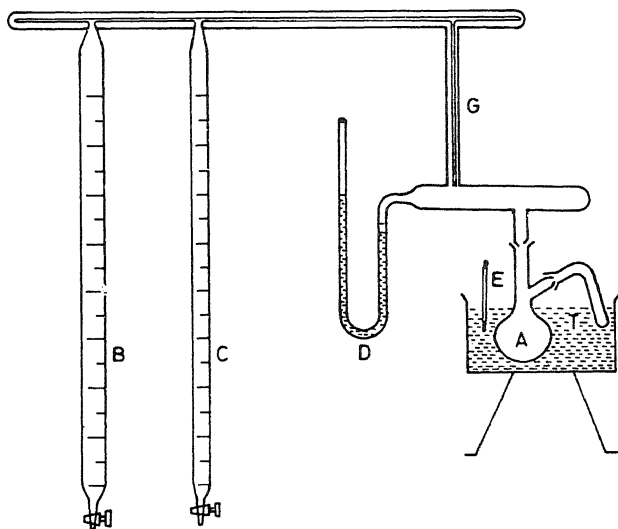


Figure 1. Experimental set-up for the determination of catalytic activity of H_2O_2 decomposition: A—reaction vessel; B—50 ml burette; C—10 ml burette; D—manometer; E—thermometer; T—thermostat; G—capillary tube.

poured into the reaction vessel by rotating the 'V' tube through 90°. A stop watch was simultaneously started to monitor the time. The entire mixture was stirred, using a magnetic stirrer, during the course of the reaction. At regular intervals of time, the burette readings were noted which indirectly measured the volume of O₂ evolved in terms of the rise of manometric liquid. In the case of ferrites, 10 mg of the sample were taken whereas in the case of cobaltites 5 mg of the sample were sufficient to study the reaction kinetics. (With 10 mg of cobaltites, the amount of O₂ evolved was so large and rapid that, in a fraction of a second the manometric liquid flew out; thus hindering proper measurements.)

3. Results and discussion

The characterization and particulate properties of ferrites and cobaltites are summarized in table 1. The XRD data clearly show that the oxides have a spinel structure and the observed a values correspond to those reported in the literature. The crystallite sizes calculated from X-ray line broadening using Debye-Scherrer formula (Klug and Alexander 1954) are in the range of 6–24 nm. The particle size and surface area values range from 0.8–4.6 μ and 12–140 m²/g, respectively, and clearly show that the particles are very fine and therefore can be expected to be highly reactive. In fact the reactivity of these fine particles was seen in the ability of ferrite powders to achieve almost theoretical density when sintered $\sim 1000^\circ\text{C}$. However, the large surface area of these oxide materials can be expected to find application in heterogeneous catalytic reactions, and as a test, the kinetics of H₂O₂ decomposition has been investigated. As the oxides were ultrafine in nature, the kinetics of H₂O₂ decomposition could not be studied using the KMnO₄ titrimetric method (Keating *et al* 1965) because of the difficulty in the separation of the dispersed fine ferrite particles in H₂O₂.

The plots of volume of oxygen V (ml) evolved versus time t (min) for H₂O₂ (30%) decomposition in the presence of ferrite and cobaltite are shown in figures 2a & b, respectively. The specific rate constants K_s mol l⁻¹ s⁻¹ gm⁻¹ with $\pm 5\%$

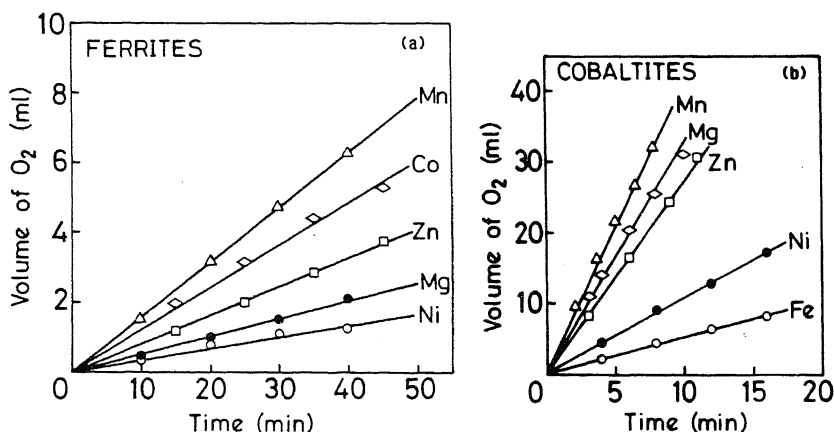


Figure 2. Decomposition of H₂O₂ (30%) on (a) ferrites, (b) cobaltites, at 30°C.

Table 2. Rate constants for H_2O_2 decomposition on ferrites and cobaltites.

Catalysts	Zero-order rate constants $K_s (\text{mol l}^{-1} \text{s}^{-1} \text{gm}^{-1})$ at 30°C	First-order rate constants $K_1 (\text{s}^{-1} \text{gm}^{-1})$ at 30°C
MnFe_2O_4	0.259	0.2612
CoFe_2O_4	0.196	0.2316
NiFe_2O_4	0.053	—
ZnFe_2O_4	0.139	—
MgFe_2O_4	0.074	0.0676
Fe_3O_4	0.0268	—
MnCo_2O_4	6.57	0.33
FeCo_2O_4	0.854	—
NiCo_2O_4	1.784	—
ZnCo_2O_4	4.49	0.2288
MgCo_2O_4	5.36	0.632
Co_3O_4	1.25	—

error, corrected for self-decomposition of H_2O_2 (30%) i.e. a blank run without the catalyst (O_2 evolution rate at 30°C $1.6 \times 10^{-4} \text{ ml s}^{-1}$) are given in table 2. A linear V - t plot is indicative of reaction kinetics which are zero order with respect to H_2O_2 .

In the second set the decomposition kinetics with 0.3% H_2O_2 was found to follow a rate law which was first order with respect to H_2O_2 . The results are shown in figures 3a and 3b, expressed in the form of a $\log V_{\max} - V_0/V_{\max} - V_t$ versus time (min) plot, where V_0 is the volume of oxygen evolved at time $t = 0$, $V_{\max}$ is the maximum volume of oxygen evolved at time (t) gave linear plots. The specific rate constants $K_s \text{ s}^{-1} \text{ gm}^{-1}$ ($\pm 5\%$ error, corrected for self-decomposition of H_2O_2) are given in table 2. The reaction rate was monitored in the initial kinetic region,

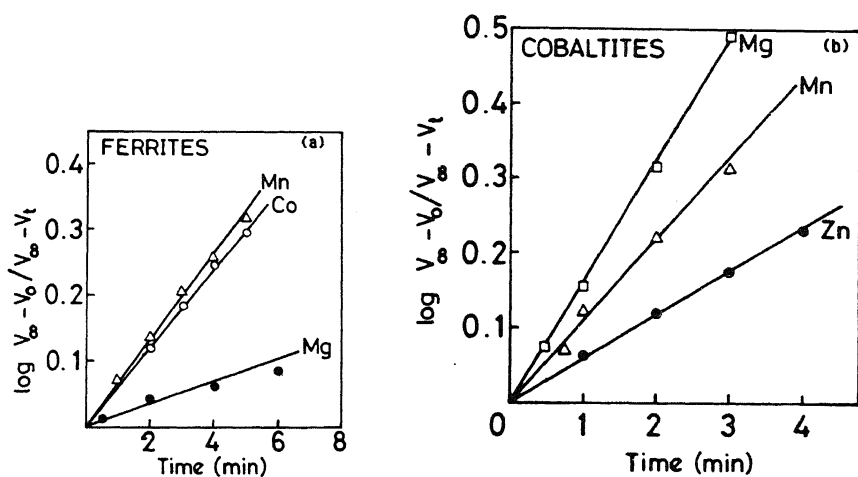
**Figure 3.** Decomposition of H_2O_2 (0.3%) on (a) ferrites, (b) cobaltites, at 30°C .

Table 3. Activation energies for ferrites and cobaltites.

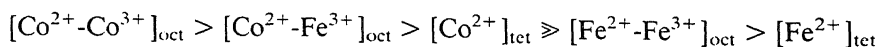
Catalyst	Rate constant $K \text{ s}^{-1} \text{ g}^{-1}$			E_a kcal/mol
	$K(308^\circ\text{K})$	$K(313^\circ\text{K})$	$K(318^\circ\text{K})$	
<i>Ferrites</i>				
MgFe_2O_4	0.056	0.099	0.120	9.15
MnFe_2O_4	0.384	0.673	0.741	12.32
CoFe_2O_4	0.305	0.360	0.47	8.39
<i>Cobaltites</i>				
MgCo_2O_4	1.87	3.12	—	16.6
MnCo_2O_4	1.08	1.3	—	11.04
FeCo_2O_4	0.078	0.086	0.096	4.19
NiCo_2O_4	0.066	0.115	0.187	19.78
ZnCo_2O_4	0.370	0.545	—	17.03

whereafter the first-order plots lose its linearity. This may be due to the formation of gas pockets in the solid catalyst which may mask the activity of potential sites as encountered earlier (Cota *et al* 1964). The reaction rate constants were found to be independent of the initial H_2O_2 concentration (0.3%) characterising the first-order kinetics.

The energy of activation for the first-order kinetics were also calculated, the values of which range from 7–19 kcal mol⁻¹ as shown in table 3.

The consequences of the reaction kinetics studied at two different concentrations: 30% and 0.3% has led to the conclusion that manganese and magnesium ferrites and cobaltites are quite promising as catalysts. The inactivity of large surface area oxides, ZnFe_2O_4 and FeCo_2O_4 , at lower concentrations of H_2O_2 (0.3%) appears to indicate that an optimum concentration of H_2O_2 is essential. This could in turn mean that the initial concentration of peroxide is also a matter of importance in governing the catalytic behaviour of the oxides.

The observed catalytic activity appears to be proportional to the surface area of the oxides. Thus a large surface area and a fine particle nature of the catalysts favour the heterogeneous decomposition of H_2O_2 . However, when comparing the order of reactivity in a given set of ferrites or cobaltites with the order of surface areas, some discrepancies are observed which can be explained in terms of the electronic structure and surface morphology of the spinels, that is, the distribution of M^{2+} and Fe^{3+} or Co^{3+} ions in the tetrahedral or octahedral sites in the spinel. Another important feature observed is that the cobaltites, having lower surface areas, are much more active than the ferrites. This may be explained in terms of the better electron-hopping ability of Co^{2+} or Co^{3+} species in the octahedral sites of spinels. The high reactivity of the MnFe_2O_4 and MnCo_2O_4 could also be speculated upon in similar terms. The redox couple $[\text{Mn}^{2+}\text{-Fe}^{3+}]$ and $[\text{Mn}^{2+}\text{-Co}^{3+}]$ appear to have even greater potentiality than



reported earlier (Goldstein and Tseung 1974).

Since most catalytic decompositions of H_2O_2 have been studied in the presence of KOH, which is known to control the reaction kinetics, a representative

experiment was done with CoFe_2O_4 using KOH. The observed rate constant ($K = 0.4545 \text{ s}^{-1} \text{ g}^{-1}$) is much higher than the value reported earlier ($K = 0.120 \text{ s}^{-1} \text{ g}^{-1}$) (Goldstein and Tseung 1974). This suggests that the fine particle ferrites and cobaltites prepared by the low temperature precursor technique have better catalytic activity than conventional oxides.

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Tetrad effects in mixed ligand lanthanide chelates. Part I: Lanthanide, EDTA/NTA, IMDA ternary systems

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MS received 2 May 1987; revised 31 August 1987

Abstract. The occurrence of tetrad effects has been studied for the variations in formation constants ($\log K_{MAL}^{MA}$) of the mixed ligand complexes of the type $[Ln(III).A.L.]$ (where $Ln(III) = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III)$ or $Dy(III)$; $A = EDTA$ or NTA ; $L = IMDA$), with the number of $4f$ electrons of the trivalent lanthanides. A differential plot method has been suggested for locating the (minor) breaks at the $4f^3-4f^4$ and $4f^{10}-4f^{11}$ stages in the $Ln(III)$ series.

Keywords. Lanthanide. EDTA/NTA. IMDA complexes; formation constants; tetrad effects; differential plot method.

1. Introduction

The occurrence of tetrad effects has been observed in the separation factors of the lanthanide $[Ln(III)]$ ions in solution (Preobrazhenskii 1959), and enthalpies/free energies of complexation of some binary $Ln(III)$ complexes (Ashcroft and Mortimer 1970). Recently the tetrad effects in Racah parameters of $Ln(III)$ ions have also been reported (Siekierski 1981). The terms 'regularities in stability constants' (Fidelis and Siekierski 1966), 'Gd-break' (McKay *et al* 1959), 'double-double effect' (Fidelis and Siekierski 1971), and 'tetrad effects' (Peppard *et al* 1969) have also been proposed by different workers in order to define the characteristic nature of the effect – the discontinuities observed in the variation of properties (such as formation constants) with the number of $4f$ electrons ($4f^n$) of the $Ln(III)$ ions. Explanations offered for the occurrence of tetrad effect seek to correlate the discontinuity with the change in coordination number (Betts and Dahlinger 1959) or hydration number (Grenthe 1964; Choppin and Graffeo 1965) of the $Ln(III)$ ions at $Gd(III)$ or with the total orbital angular momentum, L_{Ln} of the Ln elements, the so-called inclined-W hypothesis (Sinha 1975). Some of the inadequacies of these, particularly of the inclined-W hypothesis, have been pointed out by Siekierski and coworkers (Siekierski 1970, 1971, 1979, 1981; Fidelis and Siekierski 1971; Siekierski and Fidelis 1972; Mioduski and Siekierski 1975) and others (Williams 1982; Dzburinskii 1980; Poluektov *et al* 1982).

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The present work reports the occurrence of tetrad effects in the formation constants ($\log K_{MAL}^{MA}$) of mixed ligand Ln(III) chelates of the type [Ln(III).A.L.], where Ln(III) = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III) or Dy(III); A = EDTA or NTA; L = IMDA. A differential plot method is suggested for locating the minor breaks at the $4f^3$ - $4f^4$ and $4f^{10}$ - $4f^{11}$ stages in the Ln(III) series.

2. Experimental

The experimental part deals with the potentiometric determination of formation constants of the Ln(III) mixed ligand chelates. The Ln(III) nitrates (99.9% purity) were obtained from the Indian Rare Earths Ltd. Other chemicals used were of Sigma/Merck GR grade. Solutions were prepared in double distilled water. The concentrations of Ln(III) solutions were adjusted on the basis of their complexometric EDTA titrations (West 1969). The Irving-Rossotti approach (Irving and Rossotti 1953, 1954; Chidambaram and Bhattacharya 1970) was used at 25°C and ionic strength, $I = 0.2$ (mol dm⁻³, NaClO₄), for determining the formation constants. Final solution concentrations were kept at [Ln(III)] = [A] = [L] = 1.0×10^{-3} mol dm⁻³. EDTA was used as its disodium salt dihydrate and NTA as the free acid. The solutions of these two primary ligands were carefully pre-neutralised (totally) while preparing the titration sets. IMDA was used as the free acid. Titration sets were prepared by following the usual procedure (Chidambaram and Bhattacharya 1970). pH titrations were carried out on an Elico digital pH meter (model LI-120) reading upto 0.01 pH unit and a micro-burette with an accuracy of 0.01 ml using a 0.2 mol dm⁻³ carbonate-free NaOH. Reproducible pH data were used for evaluating the formation constants. The experimental values of the formation constants were refined statistically by the *Q*-test (Pecsok *et al* 1976) and algebraically by the linear plot method (Rossotti and Rossotti 1955). Formation constants $\log K_{ML}^M$, $\log K_{ML_2}^{ML}$ and $\log K_{MAL}^{MA}$ (the terms have their usual meaning) are presented in table 1. The quantities in parentheses represent the precision of the values in the form of standard deviations.

3. Results and discussion

The formation constant data give two additional stability quantifying parameters $\Delta \log K_1 (= \log K_{MAL}^{MA} - \log K_{ML}^M)$ and $\Delta \log K_2 (= \log K_{MAL}^{MA} - \log K_{ML_2}^{ML})$, which have been recorded in table 1.

In the present ternary systems ($M + A \rightleftharpoons MA$; $MA + L \rightleftharpoons MAL$) it has been noticed that for the ML binary systems precipitation occurs at pH ~ 6.5 , but for the ternary MAL systems this pH is raised to ~ 8.5 - 8.9 for NTA, and no precipitation takes place with EDTA even upto pH 11. This may be regarded as evidence for the formation of sufficiently stable ternary chelates. The binary chelates MA are formed at pH ~ 3 and remain stable over a wide pH range (upto ~ 7.5 with NTA and ~ 8.5 with EDTA) as may be seen from a representative set of titration curves for the ternary system [Eu(III). EDTA. IMDA] (figure 1).

Table 1. Formation constants, $\log K_{ML}^M$, $\log K_{ML_2}^M$, $\log K_{ML_2}^{MA}$ and $\Delta \log K_1$ and $\Delta \log K_2$ values of the binary and ternary lanthanide complexes.
Temperature = 25°C; ionic strength, $I = 0.2(\text{mol dm}^{-3}, \text{NaClO}_4)$

Formation constants and $\Delta \log K$	Values of formation constants and $\Delta \log K$ for Ln(III) ions									
	La (4f ⁰)	Ce (4f ¹)	Pr (4f ²)	Nd (4f ³)	Sm (4f ⁵)	Eu (4f ⁶)	Gd (4f ⁷)	Tb (4f ⁸)	Dy (4f ⁹)	
$\log K_{ML}^M$ (L = IMDA)	6.30 (± 0.03)	6.41 (± 0.02)	6.55 (± 0.02)	6.70 (± 0.03)	6.86 (± 0.03)	6.91 (± 0.03)	6.78 (± 0.02)	7.06 (± 0.04)	7.16 (± 0.04)	
$\log K_{ML_2}^M$	4.80 (± 0.03)	4.88 (± 0.01)	4.91 (± 0.01)	5.09 (± 0.03)	5.53 (± 0.03)	5.58 (± 0.02)	5.53 (± 0.02)	5.68 (± 0.02)	5.74 (± 0.02)	
$\log K_{MAL}^{MA}$ (A = NTA)	5.37 (± 0.02)	5.49 (± 0.01)	5.54 (± 0.01)	5.81 (± 0.01)	5.86 (± 0.02)	5.94 (± 0.02)	5.76 (± 0.02)	6.13 (± 0.03)	6.24 (± 0.03)	
$\Delta \log K_1$	-0.93	-0.92	-1.01	-0.89	-1.00	-0.97	-1.18	-0.93	-0.92	
$\Delta \log K_2$	+0.57	+0.61	+0.63	+0.72	+0.33	+0.36	+0.23	+0.45	+0.50	
$\log K_{MAL}^{MA}$ (A = EDTA)	3.97 (± 0.02)	4.17 (± 0.02)	4.28 (± 0.02)	4.37 (± 0.02)	4.47 (± 0.02)	4.58 (± 0.02)	4.44 (± 0.03)	4.68 (± 0.03)	4.85 (± 0.03)	
$\Delta \log K_1$	-2.33	-2.24	-2.27	-2.32	-2.39	-2.33	-2.34	-2.34	-2.31	
$\Delta \log K_2$	-0.83	-0.71	-0.63	-0.71	-1.06	-1.00	-1.09	-1.00	-0.89	

Note: The values in parentheses below formation constants indicate standard deviation.

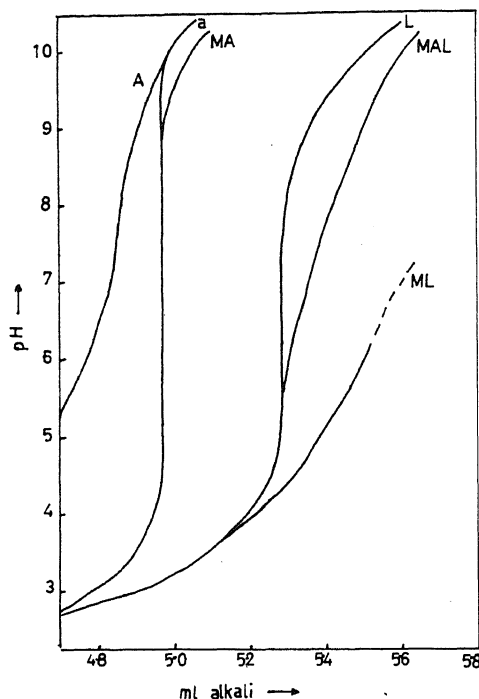


Figure 1. Representative pH titration plots for the ternary system [Eu(III).EDTA.IMDA]. Curves: a = $\text{HClO}_4 + \text{NaClO}_4$, L = $\text{HClO}_4 + \text{NaClO}_4 + \text{IMDA}$, A = $\text{HClO}_4 + \text{NaClO}_4 + \text{EDTA}$, MA = $\text{HClO}_4 + \text{NaClO}_4 + \text{EDTA} + \text{Eu(III)}$, ML = $\text{HClO}_4 + \text{NaClO}_4 + \text{IMDA} + \text{Eu(III)}$, MAL = $\text{HClO}_4 + \text{NaClO}_4 + \text{Eu(III)} + \text{EDTA} + \text{IMDA}$ (total volume = 50 ml).

Analysis of the tabulated data shows that the $\Delta \log K_1$ values are negative with A = NTA as well as EDTA; the values with EDTA are more negative. Also the sequence in $\log K_{\text{MAL}}^{\text{MA}}$ values is consistently $\text{NTA} > \text{EDTA}$, which is the opposite of the known order, $\text{EDTA} > \text{NTA}$ for the binary $[\text{Ln(III).A}]$ chelates (Ashcroft and Mortimer 1970). These trends may be largely a consequence of electrostatic effect. With NTA the primary complex MA is neutral, $[\text{Ln(III)NTA}]^0$ and that with EDTA is negatively charged, $[\text{Ln(III)EDTA}]^-$. The addition of the secondary ligand, IMDA^{2-} involves electrostatic repulsion with EDTA and hence lowers its $\log K_{\text{MAL}}^{\text{MA}}$ values below those with NTA. The $\Delta \log K_1$ values are evidently negative due to the same electrostatic effect ($\log K_{\text{ML}}^{\text{M}} > \log K_{\text{MAL}}^{\text{MA}}$), which shows up prominently with EDTA so that numerically $\Delta \log K_1(\text{EDTA}) > \Delta \log K_1(\text{NTA})$. In accordance with the 'total effect' (Bjerrum 1941) it is observed that for the IMDA chelates $\log K_{\text{ML}}^{\text{M}} > \log K_{\text{ML}_2}^{\text{ML}_2}$. Since mathematically $\Delta \log K_2 - \Delta \log K_1 = \Delta \log K_L (\log K_{\text{ML}}^{\text{M}} - \log K_{\text{ML}_2}^{\text{ML}_2})$, we get the order $\Delta \log K_2 > \Delta \log K_1$ as is clear from table 1.

We now proceed to discuss the occurrence of the tetrad effects. The observed stability sequence for ML, ML_2 as well as for MAL chelates with respect to the Ln(III) ions is $\text{La} < \text{Ce} < \text{Pr} < \text{Nd} < \text{Sm} < \text{Eu} < \text{Gd} < \text{Tb} < \text{Dy}$. The pattern of variation in $\log K$ values is seen clearly from the plots of the formation constants $\log K_{\text{ML}}^{\text{M}}$, $\log K_{\text{ML}_2}^{\text{ML}_2}$ or $\log K_{\text{MAL}}^{\text{MA}}$ vs. $4f^n$, i.e. the number of $4f$ electrons in the

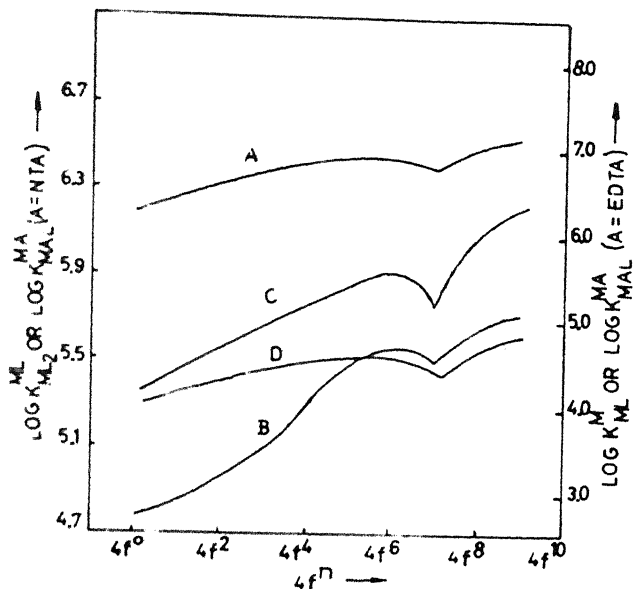


Figure 2. Variation in formation constant values with the number of $4f$ electrons of Ln(III) ions. Curve A: $\log K_{\text{ML}}^{\text{MA}}$; Curve B: $\log K_{\text{ML}}^{\text{MI}}$; Curve C: $\log K_{\text{ML}}^{\text{MA}}$ ($A = \text{NTA}$); Curve D: $\log K_{\text{ML}}^{\text{MA}}$ ($A = \text{EDTA}$).

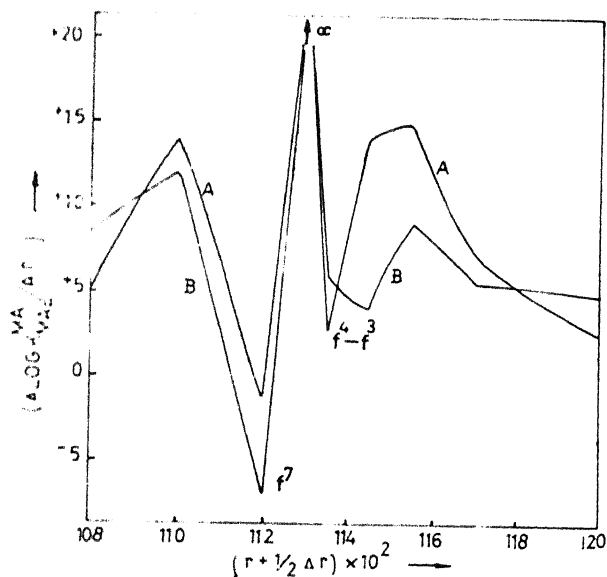


Figure 3. Differential plots showing variation in $(\Delta \log K / \Delta r)$ with $(r + \frac{1}{2} \Delta r) \times 10^2$ for the Ln(III) chelates. Curve A: $[\text{Ln(III).IMDA}]$; Curve B: $[\text{Ln(III).EDTA.IMDA}]$.

ions (figure 2). A consistent dip at Gd(III) , i.e. the half-filled shell stage, and end of the second tetrad is a prominent manifestation of the tetrad effect. (possible) occurrence of a minor break at the $4f^3$ - $4f^4$ stage, i.e. the end of the first tetrad (and another at the $4f^{10}$ - $4f^{11}$ stage, i.e. the end of the third tetrad, which

we have not been able to study here due to non-availability of the higher lanthanides is not visible from the plots in figure 2. We suggest the use of 'differential plots' for locating these minor breaks. A differential plot is obtained by plotting the differences, $\Delta \log K$ between $\log K$ values of two successive Ln(III) ions divided by the corresponding differences in their ionic radii, r (Goldschmidt values), $(\Delta \log K / \Delta r)$ vs. $(r + \frac{1}{2} \Delta r)$. Representative differential plots for the binary [Ln.(III) IMDA] and ternary [Ln.(III) EDTA.IMDA] systems are shown in figure 3. These plots show a clear dip at the $4f^3$ - $4f^4$ stage also besides a very prominent depression at Gd(III) ($4f^7$). In all these cases where the rate of change of the property (here $\log K$), with respect to the ionic radii of the Ln(III) ions, gradually increases/decreases and reaches an extremum at the three stages $4f^3$ - $4f^4$, $4f^7$ and $4f^{10}$ - $4f^{11}$ the discontinuities become well marked at these stages in the differential plots. In such cases the differential plot method appears to be more powerful than the straight line approximation technique (Siekierski 1981).

Acknowledgements

The authors express their thanks to the Head, Department of Chemistry, for encouragement and to the UGC, New Delhi, for financial assistance (MCS) and a fellowship (SV).

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2-Oximinodimedone monoguanyldiazone as spectrophotometric reagent for determination of iron

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MS received 2 March 1987; revised 18 May 1987

Abstract. The synthesis, properties and analytical possibilities of 2-oximinodimedone monoguanyldiazone as spectrophotometric reagent have been examined. A new method for the determination of iron has been developed in a concentration range varying from 0.2–5.0 ppm of iron; the molar absorptivity is 1.1×10^4 litres $\text{mol}^{-1} \text{cm}^{-1}$ at 600 nm and the relative error is $\pm 0.3\%$. The method has been applied satisfactorily to the determination of iron in different inorganic samples.

Keywords. Iron; spectrophotometric determination; 2-oximinodimedone mono-guanyldiazone.

1. Introduction

Guanyldiazones have not been extensively studied as analytical reagents. We have initiated a systematic study of these compounds in chemical analysis with pyridin-2-aldehyde guanyldiazone (PAG) (Román *et al* 1981), a compound with a pyridinic nitrogen as second electron donor group. Later, we have studied salicylaldehyde guanyldiazone (SAG) (Berzas *et al* 1984) and 2-hydroxy-1-naphthaldehyde guanyldiazone (NAG) (Salinas *et al* 1985), both compounds with a phenolic group as electron donor. In all cases, iron reacts with these compounds giving suitable coloured complexes for the spectrophotometric determination of this metal.

In this paper, following our earlier systematic study, the analytical possibilities of 2-oximinodimedone monoguanyldiazone (ODMG) are studied. This compound has an oxime group as electron donor. The reaction between ODMG and iron is studied and a new spectrophotometric method for the determination of this metal in different samples is described.

2. Experimental

2.1 Reagents and apparatus

All solvents and chemical reagents used were of analytical grade.

ODMG aqueous solutions were used at different concentrations. Standardized solutions of Fe(II) (1.002 g/l) and Fe(III) (0.992 g/l) were used. A buffer solution

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of pH 5.5 was prepared by dissolving 41 g of sodium acetate in 6 ml of acetic acid and diluting to 1 litre with demineralized water. A 0.5 M ascorbic acid solution, freshly prepared, was used.

A Zeiss DMR 11 and a Beckman DU 50 spectrophotometers, both with 1 cm glass or fused-silica cells, as well as a Crison 501 digital pH-meter with a glass-AgCl electrode, were used.

2.2 *Synthesis of 2-oximinodimedone monoguanyldiazone (ODMG)*

In order to obtain ODMG, 2-oximinodimedone was previously obtained by Haas's (1907) procedure. Two grams of powdered dimedone (5,5-dimethyl-1,3-cyclohexanedione) were dissolved in a solution of 7 g of sodium hydroxide in 30 ml of water, 30 ml of ethanol were then added, and while the solution was cooled in a freezing mixture and thoroughly stirred, 0.99 g of NaNO_2 was added and the solution was neutralized dropwise with concentrated HNO_3 to a slight excess, keeping the temperature below 10°C (during the addition of HNO_3 a blue color is observed which then changes to yellow). This cold solution was mixed with a solution of 1.95 g of aminoguanidine nitrate in 30 ml of water. The solution was stored at 4°C for 24 hr. The yellow product was collected by filtration and washed with ethanol and ether. (m.p. $133\text{--}135^\circ\text{C}$). Found: C, 34.9%; H, 5.6%; N, 27.7%. Calculated for $\text{C}_9\text{H}_{15}\text{N}_5\text{O}_2 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$: C, 35.29%; H, 5.88%; N, 27.45%.

2.3 *Recommended procedure for the determination of iron*

Into a 25 ml volumetric flask, a suitable aliquot of sample solution containing up to $125\text{ }\mu\text{g}$ of iron, 0.5 ml of 0.5 M ascorbic acid solution, 10 ml of 0.4% reagent solution and 5 ml of buffer solution were transferred, diluted to the mark with demineralized water and mixed well. The absorbance was measured at 600 nm against demineralized water, 30 min later. A suitable prepared calibration graph or empirical calculation was used to convert absorbance into concentration.

3. Results and discussion

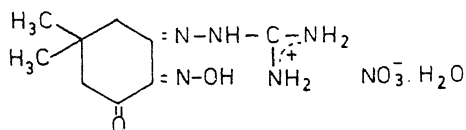
3.1 *Properties of ODMG*

3.1a Solubility: The solubility of ODMG in several solvents at room temperature was determined by Wittemberger's method (1959). ODMG is soluble in water (17 g/l) and ethanol (7 g/l) and sparingly soluble in methyl isobutyl ketone. In this work, all ODMG solutions were prepared in water.

3.1b Stability: Dilute aqueous solutions of ODMG (6.5×10^{-5} M) are stable at $3 < \text{pH} < 11$. In acid medium ($\text{pH} = 1.5$) they are not very stable. Aqueous solutions of 3.3×10^{-3} M reagent ($\text{pH} \approx 5$) are stable for at least 15 days.

3.1c Spectral characteristics: The infrared spectrum was obtained (KBr disks) and the bands were assigned (cm^{-1}) to the stretching vibrations of $\text{C}=\text{N}-\text{OH}$ (3400), $-\text{NH}-$ (3180), $\text{C}=\text{O}$ (1700), $-\text{NH}-\text{C}(=\text{NH})-\text{NH}$ (1680), $\text{C}=\text{N}$ (1590) and $-\text{C}(\text{CH}_3)_2$ (1370). The NMR spectrum was obtained in $\text{DMSO}-d_6$ with TMS as internal reference. The peaks (δ , ppm) assigned were 1.05s (protons- CH_3 groups),

2.6d (protons-CH₂-group), 3.6s (protons-NH-group) and 7.65s ($-\overset{+}{C}(\text{NH}_2)_2$ group). The ultraviolet absorption spectra in water show two maxima at 270 nm and 230 nm in acid medium and two maxima at 330 nm and 250 nm in basic medium. Taking into account the obtained spectral data, we can propose the following structure for ODMG:



3.1d Ionization constants: The ionization constants were determined by the Stenstrom and Goldsmith (1926) method at 20°C and ionic strength 0.1. The results obtained were $pK_1 = 6.65 \pm 0.22$ and $pK_2 = 10.50 \pm 0.28$. Similar results were obtained by using the potentiometric method described by Chabereck and Martell (1952): $pK_1 = 6.57 \pm 0.12$ and $pK_2 = 10.39 \pm 0.22$.

3.1e Qualitative test: The reaction of ODMG with several inorganic ions at various pH values was tested. ODMG reacts with Pd(II), Fe(III), Mn(II), Co(II), Ni(II) and V(V) giving a yellow colour, with Fe(II) giving a blue color and with Cu(II) giving a green colour. Co(II) and ODMG do not react in acid medium, but the yellow colour obtained in basic medium does not disappear when the solution is acidified. The absorption spectra of these compounds were recorded against reagent blanks and the most important results are summarized in table 1.

3.2 Spectrophotometric determination of iron

ODMG reacts in slightly acid medium with Fe(II) to form a blue complex having an absorption spectrum with λ_{max} at 600 nm. The formation of this complex is favoured in the presence of ascorbic acid and consequently, Fe(III) also can be determined if a sufficient amount of ascorbic acid is added. The blue complex formation provides a favourable analytical method for the spectrophotometric determination of this metal ion in aqueous medium. All variables were studied.

Table 1. Characteristics of ODMG compounds.

Ion	λ_{max}		ϵ
	pH	(nm)	litres $\cdot$ mol ⁻¹ $\cdot$ cm ⁻¹
Fe(II)	5.5	600	1.1×10^4
Fe(III)	9.5	440	2.9×10^3
Co(II)	9.5	435	4.8×10^3
Co(II)*	3.0	380	1.0×10^4
Mn(II)	9.5	445	3.9×10^3
Ni(II)	9.5	445	1.1×10^3

*Sample is first rendered alkaline with NaOH.

3.2a Influence of pH: Samples were prepared in 25 ml volumetric flasks containing 2 ppm of iron, 5 ml of 0.5 M ascorbic acid, 10 ml of 0.4% ODMG solution, 5 ml of 0.5 M KCl and variable amounts of HCl and NaOH in order to obtain the desired pH value. The formation of the blue Fe(II) complex is maximum and pH-independent in the range 4.8–6.8 (figure 1). A buffer acetate solution of pH = 5.5 is recommended.

3.2b Influence of the concentration of ODMG: The effect of the chromogenic reagent was examined by measuring the absorbance of solution containing 2 ppm of iron and variable amounts of ODMG. It was found that 4 ml of 0.4% (w/v) ODMG solution sufficed to complex the amount of Fe(II) taken; with higher concentrations the absorbance was essentially constant. Ten millilitres of 0.4% ODMG solution are recommended as a suitable amount of reagent.

3.2c Influence of the amount of ascorbic acid: The presence of ascorbic acid increases the formation of the blue complex and its stability in solution. This fact indicates that the blue complex can be oxidized by atmospheric oxygen; ascorbic acid inhibits this oxidation. It was found that 0.5 ml of 0.5 M ascorbic acid was sufficient to obtain maximum absorbance.

3.2d Influence of the order of addition: From experiments in which the order of addition of reagents was varied in all possible ways, it was deduced that the reaction between Fe(II) and ODMG is independent of the order of addition.

3.2e Stability of the complex: The stability of one sample containing 2 ppm of Fe(II) was studied. The absorbance at 600 nm was constant within 1% over a period of 2 hr.

3.2f Composition of the complex: Job's method was applied to the determination of the stoichiometry and the latter was found to be 1 : 3, metal : reagent. The stability constant was determined by the Holme and Langmyhr (1941) and the Jiménez *et al* (1977) methods and was found to be 3.20×10^9 .

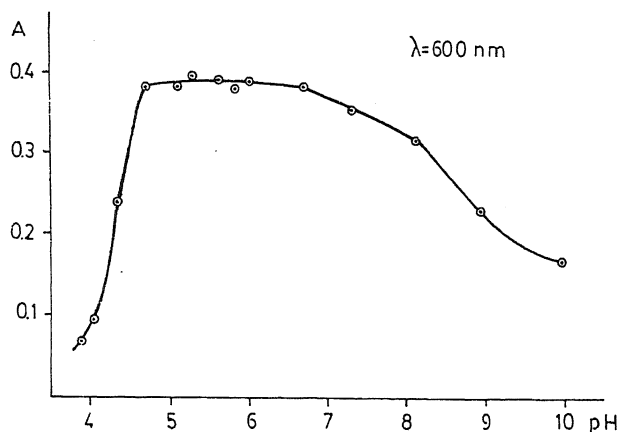


Figure 1. Influence of pH on complex formation.

3.2g Calibration and precision: The Fe(II)–ODMG complex obeyed Beer's law in the range 0.2–5.0 ppm of iron. The molar absorptivity was 1.1×10^4 litres $\cdot$ mol $^{-1} \cdot$ cm $^{-1}$ at 600 nm. The optimum working range, as evaluated by Ringbom's method was 0.9–4.0 ppm of iron. The relative error (11 determinations, 2 ppm of Fe(II), 95% confidence level) was $\pm 0.3\%$.

3.2h Interferences: The effect of diverse ions was studied for the determination of 2 ppm of iron. An error of 2% in the absorbance was considered tolerable. The results obtained are presented in table 2.

3.3 Applications

The recommended procedure has been applied satisfactorily to the determination of iron in Portland cement, magnesite, monazite, lead concentrate, zinc concentrate and manganese ore.

The samples were dissolved according to the following procedures.

Portland cement: Take about 0.1 g of the sample and 0.2 g of ammonium chloride and add 5 ml of concentrated hydrochloric acid. Heat on a steam-bath for 30 min. Add 20 ml of hot water to the solution for complete dissolution of the soluble components of the cement sample. Filter, and wash the precipitate with hot dilute hydrochloric acid and hot water. Cool the filtrate and dilute it to 100 ml in a standard flask.

Magnesite: Take about 0.5 g of the sample and dissolve it in a few ml of concentrated perchloric acid. Heat on a steam-bath to a white residue of silica. Add a few ml of water, filter, and wash the precipitate with acidified hot water. Cool the filtrate and dilute it to 100 ml in a standard flask.

Table 2. Effect of diverse ions in the spectrophotometric determination of 2 ppm of Fe(II).

Maximum tolerance diverse ion/Fe(II) ratio (w/w)	Ions
<1	V(V), Pd(II), DCTA
1	Cr(III), Ni(II), Cu(II), Sn(II), Co(II), EDTA, oxalate
3	Cr(III)*
5	Hg(II), W(VI), Al(III), Co(II)**, Bi(III), Sb(III), citrate
50	Pb(II)
100 [†]	Mn(II), Cd(II), Zn(II), Mo(VI), La(III), Mg(II), Ca(II), Sr(II), Ba(II), As(III)
250	Bromate, fluoride, thiocyanate
500	Tartrate, phosphate
1000	Thiosulphate, chlorate, triethanolamine

*In the presence of 2000 ppm of triethanolamine; **in the presence of 2000 ppm of thiosulphate; [†]maximum amount tested.

Monazite: Take about 1 g of the sample and dissolve it in a few ml of concentrated sulphuric acid. Heat for 2–3 hours. Cool, extract with 100 ml of cold water, and filter. Add 20 ml of 10 g/l fluoride solution and set aside for 3–4 hours. Filter the thorium and dilute it to 25 ml in a standard flask.

Lead and zinc concentrates: Take about 0.1 g of the sample and dissolve in a few millilitres of concentrated perchloric acid. Heat until dissolution is complete. If a white precipitate of lead sulphate is observed, filter it off and wash it with hot water. Cool the filtrate and dilute it to 100 ml in a standard flask.

Manganese ore: Take about 0.15 g of the sample and dissolve it in a few ml of concentrated hydrochloric acid. Heat on a steam-bath to a white residue of silica.

Table 3. Determination of iron in diverse samples.

Sample	Certified % composition	Fe certified (%)	Fe found (%)*
Portland cement BCS-372	SiO ₂ (21.3); TiO ₂ (0.33); CaO (65.8); Al ₂ O ₃ (5.35); MgO (1.3); Mn ₂ O ₃ (0.06); Na ₂ O (0.21); K ₂ O (0.62); P ₂ O ₅ (0.19); SO ₃ (2.35).	1.74	1.57
Monazite BAS-71bG	ThO ₂ (6.2); CeO ₂ (21.4).	0.90 [†]	0.85
High purity Magnesite BCS-389	SiO ₂ (0.89); Al ₂ O ₃ (0.23); TiO ₂ (0.015); Cr ₂ O ₃ (0.28); MnO (0.008); CaO (1.66); MgO (96.7); Na ₂ O (0.03); K ₂ O (0.01); B ₂ O ₃ (0.029).	0.20	0.19
Low silica Magnesite chrome BCS-396	SiO ₂ (1.37); Al ₂ O ₃ (5.73); TiO ₂ (0.26); Cr ₂ O ₃ (15.6); MnO (0.17); CaO (1.12); MgO (64.6); B ₂ O ₃ (0.09).	7.62	8.04
Manganese ore BCS-176/2	SiO ₂ (2.53); Al ₂ O ₃ (5.2); TiO ₂ (0.30); CaO (0.09); MgO (0.04); S (0.018); P (0.087); Mn (47.5); Na ₂ O (0.11); K ₂ O (1.30); BaO (0.19); As ₂ O ₃ (0.22).	6.86	6.61
Zinc concentrate BAS-41 dG	Zn (51.4); S (31.2); Pb (0.91); Cu (0.10); As (0.13); Mn (1.12); Cd (0.22); CaF ₂ (0.02).	10.0	9.57
Lead concentrate BAS-42G	Zn (3.40); S (14.2); Pb (75.6); Cu (0.14); As (0.32); Mn (0.21); Sb (0.15); Bi (0.02); Ag (0.074); Au (0.016).	1.35	1.39

* Mean of 3 separate determinations; [†] determined by atomic absorption spectroscopy

Add a few millilitres of water, filter and wash with dilute hydrochloric acid, and dilute to 100 ml in a standard flask.

The results obtained for the analysis of the samples are summarized in table 3.

Acknowledgement

We thank the Comisión Asesora de Investigación Científica y Técnica del Ministerio de Educación y Ciencia de España for supporting this study (Project N. 2903-83).

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Application of galvanic stripping analysis to trace determination of tin

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MS received 26 June 1986; revised 16 January 1987

Abstract. A simple, rapid and reliable procedure for the determination of tin by galvanic stripping analysis is described. The determination includes (i) preconcentration of tin onto preformed mercury film glassy carbon electrode, and (ii) re-oxidation in open-circuit position by advantageously utilizing the localized galvanic couple formation (in the absence of external electrical field or oxidant in solution). The details of the development of such a procedure and its application to the determination of tin in pure zinc materials are discussed.

Keywords. Galvanic stripping analysis; mercury film-coated glassy carbon electrode; tin determination.

1. Introduction

The determination of trace amounts of tin was investigated by several researchers by employing a variety of electrochemical techniques. Among the various techniques reported so far, viz. DC polarographic (Cooper 1955), square-wave polarographic (Ferret and Milner 1956), AG polarographic (Bond 1970) and stripping voltametric (Kermula *et al* 1959-60; Monien and Zinke 1970; Brainina and Krepivkina 1967; Neeb and Kiehnast 1967; Olson and Adams 1963; Roe and Toni 1965; Booth and Fleet 1970; de Mars 1962), stripping voltametric technique offers several advantages in terms of sensitivity, reliability and applicability to real samples. Thus, stripping analysis techniques were successfully utilized for the determination of trace quantities of tin in zinc (Kermula *et al* 1959-60) and tin-indium alloys (de Mars 1962). A potentiometric stripping analysis procedure was reported for the determination of tin in fruit juices and soft drinks (Mannino 1982, 1983). Recently, we have described a novel electroanalytical technique—Galvanic stripping analysis (GSA)—which advantageously utilizes the localized galvanic couple formation for stripping of the deposited metals on mercury film coated glassy carbon electrode (Jaya *et al* 1985). In GSA time of stripping is proportional to the concentration of metal present in solution. This paper reports the application of the GSA technique for the trace determination of tin and in analysis of high purity zinc materials.

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2. Experimental

2.1 Reagents

All solutions were prepared in conductivity water using BDH, AR chemicals. 0.1 M standard tin(II) solutions were prepared by dissolving 2.2563 g of stannous chloride ($\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$) in 100 ml of hot 1:1 conc. HCl. Dilute solutions were prepared by further addition of 1:1 HCl.

2.2 Apparatus

A conventional 3-electrode cell with a preformed mercury film glassy carbon (prepared as described elsewhere) (Jagner 1978) working electrode (Tokai & Co., 3 mm dia), a platinum foil counter and a normal calomel electrode (NCE) as reference electrode were employed. A Wenking (Model LB 75) potentiostat coupled with a Wenking scan generator (Model VSG 72) is used for controlling the potential. A Ricadenki xy/t recorder was used to record $E-t$ profiles. All the potentials were expressed with respect to NCE and measurements were made at room temperature. All experiments were carried out under identical stirring conditions during deposition as well as stripping using a Remi Magnetic Stirrer.

2.3 Procedure

A suitable aliquot (upto 40 ml) of sample solution containing ≤ 1000 ppb of tin(II) was taken in a flask and diluted to 50 ml with conductivity water after adding 5 ml of 1 N HCl. This solution was transferred to an electrochemical cell and deaerated with N_2 for 15 min. After depositing for 4 minutes under stirred condition onto preformed mercury film glassy carbon electrode at -1.2 V, the potentiostat was kept in open circuit selection mode (where the counter is disconnected from the three-electrode cell) and GSA profiles ($E-t$) were recorded on an $x-t$ recorder. The time of stripping forms the analytical signal of GSA. A calibration graph was prepared for the determination of 10–1000 ppb of tin by the same procedure.

3. Results and discussion

Preliminary studies indicated that the tin deposited onto preformed mercury film-coated glassy carbon electrode (MFGCE) at -1.2 V from tin (II) in 0.1 N HCl medium, dissolves into the medium under open circuit stripping conditions in the absence of external currents, potential inputs or chemical oxidants. This behaviour is similar to that of cadmium as reported by us earlier (Jaya *et al* 1985). Experiments were carried out to understand the driving force behind the dissolution. The oxidative dissolution of deposited tin in open circuit conditions can be either due to the presence of impurities present in the supporting electrolyte or due to localized galvanic corrosion. The non-dissolution of tin from a tin-deposited hanging mercury drop electrode in the same supporting electrolyte rules out the possibility of impurities responsible for dissolution. This is further confirmed by the fact that the $E-t$ profiles and time of stripping are the same irrespective of the stirring rate used during stripping. On the other hand, a separate experiment was

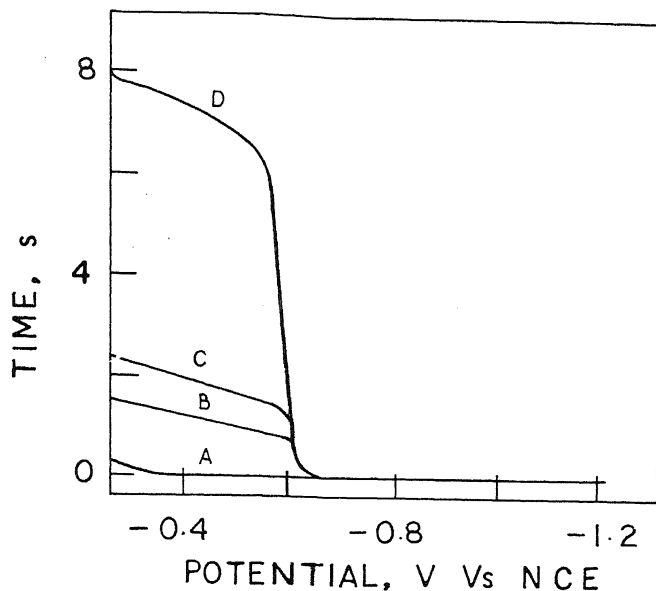


Figure 1. Galvanic stripping E - t profiles recorded for 0 , 5×10^{-7} , 10^{-6} and 5×10^{-6} M of Sn(II) (curves A, B, C and D, respectively) between MFGCE working and normal calomel reference electrode, 0.1 M HCl + 0.4 M NaCl; total volume = 50 ml; deposition potential (E_d) = -1.2 V vs NCE; deposition time (t_d) = 4 min.

conducted to confirm that localized galvanic corrosion is indeed responsible for oxidative dissolution of tin-deposited MFGCE. This was done by shifting the second reaction of the galvanic cell (i.e. evolution of H_2) by using a large area platinum foil. The observation of current flowing from large area platinum to MFGCE confirms the above contention that dissolution occurs by galvanic corrosion. Figure 1 shows the galvanic stripping potential time (E - t) profiles obtained after depositing tin from 0 , 5×10^{-7} , 10^{-6} and 5×10^{-6} M solutions (curves A, B, C and D respectively), onto MFGCE for 4 minutes at -1.2 V and subsequent stripping in open circuit position. Immediately after the deposition step, when the potentiostat is kept in open circuit position, the potential drops to ~ -0.6 V and shows a plateau on the time axis. When all the tin is dissolved from MFGCE, the potential drops slowly to OCP of MFGCE in the supporting electrolyte (viz. 0.1 V). The length of the plateau is the time required for galvanic stripping of tin and forms the analytical signal.

3.1 Effect of supporting electrolyte

The GSA profiles of 10^{-6} M of tin(II) obtained in a variety of supporting electrolyte media are furnished in table 1. The E - t profiles were drawn as described in § 2 after deposition for 4 min at -1.2 V onto MFGCE. The maximum stripping signal was obtained in 0.1 M HCl containing 0.4 M sodium chloride.

3.2 Effect of pH/H^+

The effect of pH/H^+ on GSA determination of 10^{-6} M tin(II) was studied in 0.4 M NaCl as supporting electrolyte using the MFGCE as the working electrode. The

Table 1. Effect of supporting electrolyte. Concentration of $\text{Sn(II)} = 10^{-6} \text{ M}$, $E_d = -1.2 \text{ V}$ vs NCE, $t_d = 4 \text{ min}$.

Supporting electrolyte (concentration—moles)	Stripping time (s)
HCl (0.1)	0.90
HNO_3 (0.1)	0.60
HCl (0.6)	0.70
Acetate (0.1) + NaCl (0.4)—pH2	0.35
HCl (0.1) + NaCl (0.4)	1.40
HCl (0.1) + NaNO_3 (0.4)	1.05

acidity was varied from 0.6 to 0.01 N in HCl. The results thus obtained show that the optimum acidity range is 0.15 N to pH 1.5 (cf. figure 2). Hence, pH 1 was chosen in subsequent studies.

3.3 Effect of sodium chloride

The effect of addition of varying amounts of sodium chloride (0.1 to 1.0 M) to 0.1 M HCl solution on the GSA stripping determination of tin was next investigated. As seen from table 2, the addition of 0.3 M of NaCl is essential for obtaining maximum GSA signal and is unaffected on further increase to 1 M.

3.4 Effect of deposition potential

The optimum deposition potential of tin on MFGCE was established by depositing from 10^{-6} M of tin(II) solutions for 4 min at various deposition potentials in the range -0.6 to -1.4 V vs NCE and measuring the time of stripping in GSA. As seen

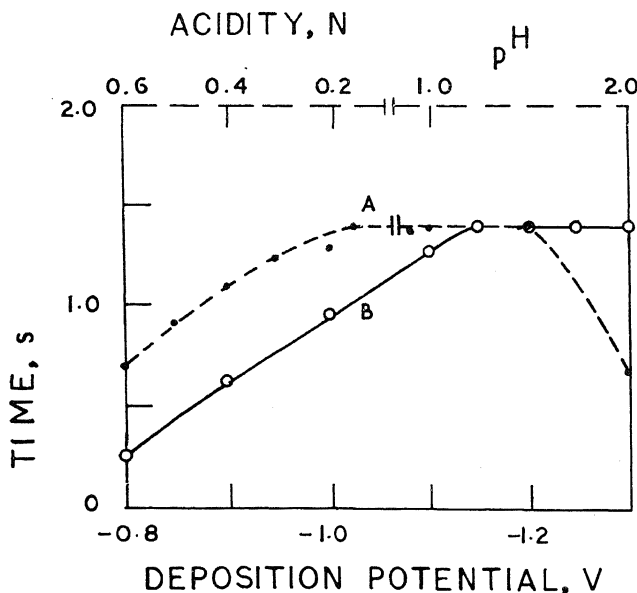


Figure 2. Effect of H^+/pH (curve A) and deposition potential (curve B) on the galvanic stripping signal of 100 ppb of Sn(II) ; 0.1 M HCl + 0.4 M NaCl, $t_d = 4 \text{ min}$.

Table 2. Effect of sodium chloride concentration. Concentration of Sn(II) = 10^{-6} M; $E_d = -1.2$ V vs NCE; 0.1 M HCl, $t_d = 4$ min.

Concentration of NaCl (M)	Stripping time (s)
0	0.90
0.1	1.25
0.3	1.40
0.5	1.40
1.0	1.40

Table 3. Analysis of zinc metal samples.

Sample solution	Amount of tin(II) added ($\mu\text{g/g}$)	Aliquot taken (ml)	Tin(II) found ($\mu\text{g/g}$)	Recovery (%)
Zinc metal (5 g per 50 ml)	—	40	0.0	—
	0.5	40	0.49	90.0
	1.0	25	1.02	102.0
	2.5	40	2.50	100.0

from curve D in figure 2, the maximum GSA stripping signal is obtained at potentials more negative to -1.15 V.

3.5 Effect of time deposition

Experiments were conducted to study the effect of deposition time (1 to 16 min) on GSA stripping signals of 10^{-6} M tin(II) using MFGCE as working electrode. The stripping signal was found to be proportional to the time of deposition suggesting the possible extension of the developed procedure for the determination of still lower concentrations of tin(II) using longer times of deposition.

3.6 Calibration graph and precision

Linear calibration graphs passing through the origin were obtained for 10–1000 ppb of tin(II) with a slope of 1.4 s/100 ppb of tin with 4 min of preconcentration time. The procedure is fairly precise, as the relative standard deviation for 5 replicate determinations of 100 ppb of tin(II) was found to be 2.3%.

3.7 Analysis of zinc metal samples

Table 3 shows the results of the determination of tin(II) in zinc metal samples by the proposed method. The data obtained on samples spiked with known amounts of tin(II) is also incorporated in the table 3. The results show the applicability of the developed procedure for the trace determination of tin(II) in zinc metal samples.

Acknowledgement

The authors wish to thank Prof. K I Vasu for his encouragement and keen interest in our work.

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Some benzimidazole amide complexes of ruthenium(II)

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MS received 30 January 1987; revised 11 May 1987.

Abstract. The synthesis and characterisation of ruthenium(II) complexes with 2-amidobenzimidazoles are reported. The complexes $\text{RuCl}_2(\text{DMSO})_4$ and $\text{RuCl}_2(\text{PPh}_3)_2$ react with 2-(acetamido)benzimidazole (AB) and 2-(benzamido)benzimidazole (BB) in acetone to give products of the type $[\text{Ru}(\text{L})_2(\text{N}-\text{O})_2]\text{Cl}_2$ [$\text{L} = \text{DMSO}, \text{PPh}_3, \text{N} \cdots \text{O} \cdots \text{AB}, \text{BB}$]. The displacement reactions are faster in the case of methyl (AB) than phenyl (BB) substituted ligands. The ligands are bifunctional chelating agents coordinating through the tertiary nitrogen of benzimidazole ring and amide oxygen. The complexes are characterised based on their elemental analysis, conductivity data, infrared, ^1H and ^{31}P nmr spectra. A *cis*-geometry is proposed for all the complexes reported.

Keywords. Ruthenium(II) complexes; benzimidazole amides; bifunctional ligands; ^{31}P and ^1H nmr; amide oxygen coordination.

1. Introduction

Metal amide complexes are an important class of coordination compounds and are currently drawing more attention since studies on these complexes help in understanding the mode of binding of the amide group in some of the closely related biological systems (Sigel and Martin 1982; Collins *et al* 1983; Che *et al* 1986). Also the coordination chemistry of chelate ligands having mixed functional groups has been extensively studied (Hedden and Roundhill 1985). An important outcome of this work is the development of hybrid ligands where one arm of the chelate will selectively bind to the metal ions and the hinging arm available for ready substitution (Hedden and Roundhill 1985, 1986; Rauchfuss and Roundhill 1973, 1974; Hedden *et al* 1984).

With the reports on the synthesis of platinum group metal complexes as anti-tumour agents containing various ligands have not been sufficient, the synthetic and structural aspects of some new and related complexes are of great interest. As part of a broad programme on the study of platinum group metal complexes with bifunctional ligands, we have undertaken the synthesis of some potential bidentate ligands, 2-(amido)benzimidazoles and their complexes with ruthenium(II). Recently we have reported the synthetic and structural aspects of some new carboxylate amide complexes with a low-valent platinum group metal ion, ruthenium(II) (Ravindar *et al* 1984). In continuation of our earlier work, we

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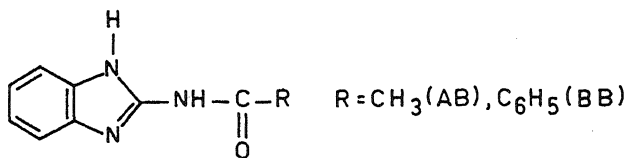


Figure 1. Structure of the ligand used in this work.

report in this paper the synthesis and characterisation of new chelate complexes of 2-(amido)benzimidazoles with both the tertiary nitrogen atom of the benzimidazole ring and the amidic oxygen complexed to ruthenium(II). The ligands used in this investigation are represented by the structure given in figure 1.

2. Experimental

Elemental analyses of C, H and N were done by microanalytical laboratory, CDRI, Lucknow, India. Magnetic measurements, conductivity and melting point determinations and infrared studies in KBr disc were carried out as reported earlier (Ravindar *et al* 1984). ^1H NMR spectra were recorded on saturated CDCl_3 solutions of complexes on Jeol FX 90. The ^{31}P $\{^1\text{H}\}$ nmr spectra in DMSO were recorded as reported earlier (Taqui Khan *et al* 1986).

The precursor materials, $\text{RuCl}_2(\text{DMSO})_4$ (Evans *et al* 1973) and $\text{RuCl}_2(\text{PPh}_3)_3$ (Stephenson and Wilkinson 1966) were prepared by published methods. All analytical data are collected in table 1. Some important IR bands are compiled in table 2.

2.1 Synthesis of ligands

The ligands 2-(acetamido)benzimidazole (AB) and 2-(benzamido)benzimidazole (BB) were prepared by the reactions of the appropriate acid halides with 2-(amino)benzimidazole in pyridine (Bellasio *et al* 1973; Skaletsky 1971). The compound 2-(amino)benzimidazole was prepared by reacting cyanogen bromide with *o*-phenylenediamine (OPDA) by stirring for several hours (Pierron 1919; Wright 1951).

2.2 Preparation of complexes

- 1 Bis (dimethylsulphoxide)bis{2-(acetamido)benzimidazole} ruthenium(II) chloride;
- 2 Bis (dimethylsulphoxide)bis{2-(benzamido)benzimidazole} ruthenium(II) chloride

Complexes 1 and 2 were obtained by the addition of 3 mmol excess of AB (0.22 gm) and BB (0.32 gm), respectively, dissolved in acetone to a refluxing suspension of the yellow complex, $\text{RuCl}_2(\text{DMSO})_4$ (0.2 gm; 0.4 mM). The colour of the solution changed from light to deep yellow (AB) and yellow orange (BB). The reaction mixtures were heated for 4–5 hours when the bulk of the complex had separated as yellow crystals. The crystals were washed with hot acetone and

Table 1. Physical data of ruthenium(II) complexes with bifunctional ligands.

Complex	Colour	M.P. (°C) ^a	μ_{eff}	Analysis (%) ^b			λ_{∞} (S cm ² mol ⁻¹)
				C	H	N	
[Ru(DMSO) ₂ (AB) ₂ Cl ₂]	Yellow	187	Diamagnetic	32.8 (31.85)	2.70 (2.65)	12.54 (12.38)	90
[Ru(DMSO) ₂ (BB) ₂ Cl ₂]	Pale yellow	193	"	48.60 (47.88)	3.96 (3.99)	10.20 (10.47)	94
[Ru(PPh ₃) ₂ (AB) ₂ Cl ₂]	Yellow	200	"	62.10 (62.18)	4.66 (4.60)	8.00 (8.06)	85
[Ru(PPh ₃) ₂ (BB) ₂ Cl ₂]	Red- brown	214	"	64.80 (65.64)	4.70 (4.78)	7.92 (7.17)	83

^a Decomposition temperatures; ^b Calculated values in parentheses.

methanol repeatedly and dried under vacuum Yields: 0.16 gm (57%) (1); 0.11 gm (33%) (2).

3 Bis(triphenylphosphine)bis{2-(acetamido)benzimidazole} ruthenium(II) chloride;

4 Bis(triphenylphosphine)bis{2-(benzamido)benzimidazole} ruthenium(II) chloride.

To refluxing acetone solutions of AB (0.11 gm; 6.3 mM) and BB (0.15 gm, 6.3 mM), solid RuCl₂(PPh₃)₃ (0.2 gm; 2.1 mM) was added and the resulting suspensions were refluxed to give clear light yellow (AB) and dark green (BB) solutions in about 20 minutes. When the solutions were refluxed for about 3 hours, complexes 3 and 4 were deposited as yellow (AB) and red brown (BB) crystals. The crystalline products were filtered and washed with hot acetone and methanol. Yields: 0.12 gm (55%) (3); 0.06 gm (25%) (4).

3. Results and discussion

The reactions of RuCl₂(DMSO)₄ and RuCl₂(PPh₃)₃ with both the ligands AB and BB were fast and gave cationic complexes of the type [Ru(L)₂(N-O)₂]Cl₂[L = DMSO, PPh₃; N-O = 2-(acetamido)benzimidazole (AB); 2-(benzamido)benzimidazole (BB)]. The yields are high when R is a methyl rather than a phenyl group. The cationic nature of the complexes was confirmed by the observed conductivity of the complexes in DMSO which is typical of a 1:2 electrolyte (Geary 1971) (table 1). Conductivity values of complexes when measured even 24 hours after their dissolution showed no changes, suggesting no rearrangement of the complexes in DMSO solution despite the strong donor capacity of the solvent.

The complexes are crystalline solids, stable in atmospheric conditions, soluble in DMSO, DMF and trifluoroacetic acid and to a large extent in chloroform.

Table 2. Some important IR spectral data for new benzimidazole amide complexes of ruthenium.

Complex	ν (N-H)	ν (C=O)	ν (C=N) ring	ν (S=O)	ν (Ru-P)
AB	3320(<i>m</i>)	1680(<i>s</i>)	1580(<i>s</i>)	—	—
BB	3310(<i>m</i>)	1658(<i>s</i>)	1560(<i>s</i>)	—	—
1.	3315(<i>m</i>)	1640(<i>s</i>)	1590(<i>m</i>)	1080(<i>s</i>) 1105(<i>sh</i>)	—
2.	3318(<i>m</i>)	1635(<i>s</i>)	1595(<i>m</i>)	1080(<i>s</i>) 1110(<i>sh</i>)	—
3.	3315(<i>m</i>)	1655(<i>s</i>)	1595(<i>s</i>)	—	515(<i>s</i>)
4.	3320(<i>m</i>)	1630(<i>s</i>)	1585(<i>m</i>)	—	520(<i>s</i>)

Key: *s* = strong; *m* = medium; *sh* = shoulder.

Considering the capacity of platinum group metals to form complexes with nitrogen containing ligands, it may be assumed that the tertiary nitrogen of the benzimidazole functionality of the ligand will be bound with the metal invariably in all the complexes. Studies on the complexation of imidazoles and benzimidazoles have also revealed that the tertiary nitrogen rather than the secondary nitrogen is the bonding site to the metal (Ghosh *et al* 1977). The characteristic absorptions in the IR which could be monitored for diagnostic assignments in the ligand before and after coordination to the metal have been compared in order to confirm the site of coordination in ligands. In the infrared spectra of ligands AB and BB, strong bands due to $\nu(\text{C}=\text{N})$ of the benzimidazolyl ring are observed at 1580 and 1560 cm^{-1} respectively. It is found in the complexes 1–4 that the position of $\nu(\text{C}=\text{N})$ is shifted to higher frequency by 15–35 cm^{-1} indicating that the bonding of benzimidazole takes place through the tertiary nitrogen atom only (Ghosh *et al* 1977) (table 2). The region 400–450 cm^{-1} assignable to $\nu(\text{M}-\text{N})$ modes contains many ligational bands, therefore the bands due to $\nu(\text{M}-\text{N})$ cannot be assigned with certainty.

In the ligands, the ring $\nu(\text{N}-\text{H})$ and amido $\nu(\text{N}-\text{H})$ together give rise to a sharp medium band in 3310–3320 cm^{-1} . The coincidence of these bands is typical for organic molecules containing both secondary amide and 2-imidazolyl or 2-benzimidazolyl groups. The position of the $\nu(\text{N}-\text{H})$ bands in the complexes, however, are almost unchanged from those in the corresponding free ligands AB and BB, which confirms the inability of the amide nitrogen from coordination. In the infrared spectra of all the complexes, the amide I band, which is to a large extent $\nu(\text{C}-\text{O})$, shifts to a lower frequency and this indicates amide oxygen coordination (Chapman and Vagg 1979; Chapman *et al* 1981; Mulqui *et al* 1982). The ligands form stable six-membered chelates through pyridine nitrogen and amidic oxygen in all the complexes.

The presence of DMSO in complexes 1 and 2 was characterized by its $\nu(\text{S}=\text{O})$, which decreases when it is coordinated through oxygen and increases upon binding to the metal through sulphur (Gopalakrishnan and Patel 1967; Reynolds 1970). The infrared spectra of complexes 1 and 2 show strong bands due to $\nu(\text{S}=\text{O})$ in the region 1050–1100 cm^{-1} and correspond to the S-bonded DMSO ligands (Evans *et al* 1973; Reynolds 1970) (table 2). The bands in this region appear to have

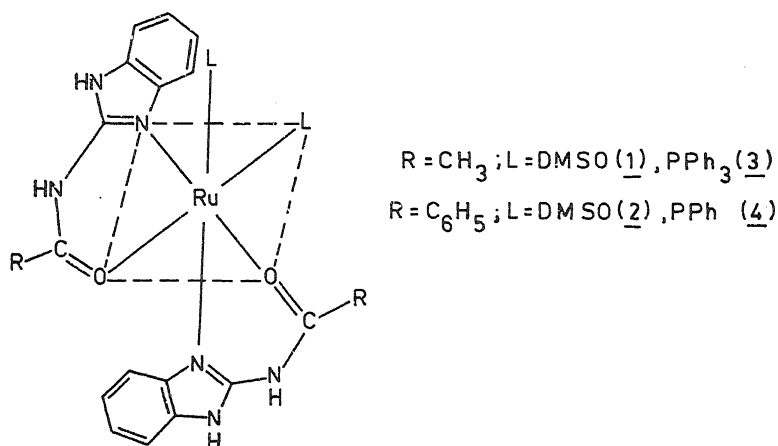


Figure 2. Structure with two non-equivalent ligands complexed in a *cis*-manner.

shoulders on the higher frequency side which may probably suggest that the two DMSO groups are coordinated in a *cis*-manner. Complexes 3 and 4 display strong bands in the far IR spectra at 520 and 515 cm^{-1} corresponding to $\nu(\text{Ru}-\text{p})$. The region 275–350 cm^{-1} is devoid of any bands confirming the total displacement of chlorides from the coordination sphere.

The ^1H nmr spectra of complexes show significant shifts due to coordination. The peaks observed in the range 3.0–3.5 δ are broad and correspond to CH_3 protons of S-bonded DMSO groups in complexes 1 and 2 (Evans *et al* 1973). Another singlet resonance at 2.33 δ due to CH_3 protons of AB ligand undergoes a downfield shift to 3.2 δ in complex 1. This observation can be interpreted on the basis of amidic oxygen coordination. Similarly, a large downfield shift of 1.37 ppm is observed for methyl protons in the ^1H nmr spectrum of complex 3. The aromatic proton resonances of benzimidazolyl ring of the ligands and PPh_3 groups absorb in the range 7.12–8.02 δ as complex multiplets and remain almost unchanged in the complexes. The resonances due to the solvent and concentration dependent amide protons of both the ligands and complexes in CDCl_3 were not observed in the range 0–10 ppm. However, addition of D_2O and recording the spectra after 24 hours caused the appearance of characteristic HOD signal at 5.0 δ (Kemp 1975). The ^{31}P nmr spectra recorded for complexes 3 and 4 in DMSO show the presence of two types of PPh_3 groups complexed to ruthenium(II). The resonances are shifted downfield by some 45–58 ppm from the free phosphine resonance at –5.2 ppm (Garrou 1981). The observation of two singlets at 51.89 and 40.63 ppm in ^{31}P nmr of complex 3 and 52.6 and 41.9 ppm in complex 4 requires a structure with two non-equivalent phosphorus ligands complexed in a *cis*-manner (figure 2).

It is well-established that amide groups must remain planar, as far as possible, even after binding to the metal (Freeman 1973). In fact the metal amide oxygen bond is weak in complexes since amide-oxygen is weakly basic, but the overall stability of complexes 1–4 is enhanced because of the closure of a six-membered chelate ring with the adjacent benzimidazolyl ring nitrogen. The amide nitrogen

binds to a metal ion only under the conditions of a deprotonation since the process of deprotonation makes nitrogen available for metal coordination without loss of the amide group resonance (Sigel and Martin 1982; Freeman 1973). However, deprotonation of ligands AB and BB and consequent complexation with ruthenium (II) have not yielded any stable chelates. This may be due to the formation of 4-membered rings which are untenable, particularly in the case of large metal ions like ruthenium(II).

Acknowledgement

One of us (TS) is thankful to CSIR, New Delhi, for the award of a research fellowship. We are grateful to Prof. M M Taqui Khan, CSMCRI, Bhavnagar, Gujarat, for his constant encouragement. Thanks are also due to Prof. K Kondal Reddy and his research group for their help in the synthesis of ligands.

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On the behaviour of small clusters near the spinodal decomposition[†]

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MS received 1 April 1987

Abstract. The canonical average of the Boltzmann factor of the interaction potential, as measured by a test particle, is shown to be equal to the inverse of the fraction of the average number ($\bar{m}_1$) of 1-particle Mayer clusters. The potential distribution theory is used to derive an analytic expression for a mean number of small clusters ($\bar{m}_n$, $1 \leq n < N$, in an N -particle system) in the mean-field expression. Near the spinodal density, the average number of small clusters undergo a sharp change. Computation of pressure shows that only the first four clusters produce surprisingly good agreement with known pressure even beyond the spinodal density.

Keywords. Behaviour of small clusters; spinodal decomposition; interaction potential; Mayer clusters; spinodal density; mean-field theory.

1. Introduction

The mean number, $\bar{m}_1$, of 1-particle clusters plays a very important role in the theories of nucleation and metastability (Becker and Doring 1935; Abraham 1971; Kalos *et al* 1978; Penrose and Lebowitz 1979; Shing and Gubbins 1981 & Garcia and Soler Torraja 1981). In the statistical mechanical theories of nucleation, the mean numbers $\bar{m}_n$ of the larger clusters are usually written in the following form (Abraham 1971)

$$\bar{m}_n = \bar{m}_1 \exp [-\Delta F(n, p, T)/k_B T], \quad n \geq 2, \quad (1)$$

where $\Delta F(n, p, T)$ is the difference between the free energy of a cluster of n particles and that of a vapour of n monomers at temperature T and pressure p . Equilibrium solutions of the Becker-Doring type of kinetic equation theories of nucleation also give $\bar{m}_n$ in terms of $\bar{m}_1$ (Becker and Döring 1935; Penrose and Lebowitz 1979),

$$\bar{m}_n = C_n (\bar{m}_1)^n, \quad (2)$$

where C_n is a function of the size n of the cluster. Recent computer simulations (Penrose and Lebowitz 1979) of cluster size distribution on lattices have also re-emphasized the importance of $\bar{m}_1$ in the nucleation process.

It is well-known that there is no unique way to define a cluster for continuous systems, although there exist several different prescriptions for doing so. These prescriptions differ from each other in some fundamental aspects, but it is believed that well below the critical temperature, when the attractive forces are important, these different prescriptions give qualitatively the same result. Recently it has been shown that the mean cluster size distribution (Bagchi 1980; Donoghue and Gibbs 1981; Gibbs *et al* 1981), defined by a reformulation of Mayer's theory of condensation (Mayer and Mayer 1980), can successfully describe the condensation process. Below the critical temperature, the cluster integrals are positive and a mean number of Mayer clusters of certain size can be defined rigorously. However, the clusters arising in the Mayer theory may not always be interpreted as an aggregate of molecules, the members of which remain within the sphere of influence of each other for a time appreciably larger than the duration of a bimolecular collision time. This is especially true at high temperatures. The formulation of a satisfactory definition of physical cluster concept has drawn considerable attention in recent years (Lee *et al* 1973; Gills *et al* 1977; Powless 1980; Lockett 1980). In this paper, however, we consider only the Mayer clusters and show that an expression like (2) can also be derived for Mayer clusters in the mean-field approximation. It is interesting to find that the Mayer clusters, which are usually called mathematical clusters because of their apparent lack of physical reality, *can so easily be substituted for physical clusters*. We have already seen that near the condensation density the size distribution of these mathematical clusters suddenly becomes bimodal, signalling the appearance of large clusters in the system. Thus, these "mathematical" clusters seem to parallel the real physical clusters in more than one respect.

In this paper, we present the following results. We demonstrate that the canonical average of the Boltzmann factor of the interaction potential (Widom 1963; Hansen and McDonald 1976), $\langle \text{BFT} \rangle$, as measured by a test particle, is equal to the inverse of the fraction of the mean number $\bar{m}_1$ of 1-particle Mayer clusters. Since recent advances in computer simulations have made it possible to calculate $\langle \text{BFT} \rangle$ directly (Adams 1974; Romano and Singer 1979), our result could be of use in computing $\bar{m}_1$. Mean-field approximations to $\langle \text{BFT} \rangle$, as developed by Widom (1963), is then used to derive an analytic expression for $\bar{m}_1$. In the limit of infinite system at fixed density, an accurate expression for the mean number of clusters $\bar{m}_n$ ($n \geq 2$) can be derived for clusters whose sizes are much smaller than the total number of particles in the system. We find that the $\bar{m}_n$ undergo a sharp change near the spinodal density. We have also computed the pressure from the mean number of these clusters and found that even by including only the first four clusters, good agreement with the exact pressure can be obtained even beyond the spinodal density.

In the next section, we derive the expressions necessary to evaluate $\bar{m}_n$. In §3, we present the results. Section 4 concludes with a brief discussion.

2. Theory

In the potential distribution theory (Hansen and McDonald 1976; Widom 1963), an expression for the canonical average of the Boltzmann factor of the interaction

energy of a test particle with all other particles of the system is derived. The configurational partition function Z_N for a system of N -particles is given by

$$Z_N = \frac{1}{N!} \int \dots \int \exp [-\beta U_N] d\tau_1 \dots d\tau_N, \quad (3)$$

where U_N is the energy of interaction of N -particles, τ_i is the element of volume of particle i and $\beta = (k_B T)^{-1}$, T being the temperature and k_B the Boltzmann constant.

Equation (3) can also be written in the following form

$$Z_N = \frac{V}{N!} \int \dots \int \exp [-\beta (U_{N-1} + \psi)] d\tau_1 \dots d\tau_{N-1}, \quad (4)$$

where one of the particles is labelled as a test particle and ψ is the energy of interaction between this test particle and the rest of the system. Equation (4) can be written in the form (Hansen and McDonald 1976).

$$Z_N = \frac{V}{N!} (N-1)! Z_{N-1} \langle e^{-\beta \psi} \rangle, \quad (5)$$

where $\langle \dots \rangle$ indicates a canonical average in the $(N-1)$ particle system.

An interesting relation, which is inverse of (5), has recently been derived

$$Z_{N-1} = \frac{N!}{V(N-1)!} Z_N \langle \langle e^{\beta \psi} \rangle \rangle, \quad (6)$$

where $\langle \langle \dots \rangle \rangle$ is a canonical average in the N -particle system and the particle that experiences the potential ψ is one of the N -particles and *not* a test particle.

We will discuss Widom's mean-field approximation to (BFT) later. First, let us show how (5) can be used to relate BFT to the mean number $\bar{m}_1$ of one particle clusters.

We start with the Mayer-Ursell cluster expansion (Mayer and Mayer 1980) for the function Z_N , given by

$$Z_N = \sum_{\{m_l\}} \prod_{l=1}^N \frac{[V b_l(T, V)]^{m_l}}{m_l!}, \quad (7)$$

$$\text{with } \sum_{l=1}^N l m_l = N. \quad (7a)$$

The $b_l(T, V)$ is the l th connected cluster integral and m_l 's are positive integers or zero. Recently it has been shown that the cluster expansion (7) is related to a general class of polynomials known as the Bell-polynomials (Gibbs *et al* 1981). These polynomials arise in the task of simplifying the n th derivative of a composite function.

As long as the b_l 's are positive, a mean number $\bar{m}_k$ for the population of the clusters of size k can be defined as (Donoghue and Gibbs 1981; Gibbs *et al* 1981; Hill 1956);

$$\bar{m}_k(T, V, N) = \sum_{\{m_l\}} m_k \prod_{l=1}^N \frac{(Vb_l)^{m_l}}{m_l!} / Z_N(T, V), \quad (8)$$

$$\sum_{l=1}^N l m_l = N.$$

We note that as long as b_l 's are positive, the statistical weight factor

$$\prod_{l=1}^N (Vb_l)^{m_l}/m_l! \text{ is well defined.}$$

There is considerable amount of controversy in the literature (Hill 1956) over the nature of the clusters as defined through (8). Above the critical temperature, $b_l(T, V)$ may become negative and $\bar{m}_k$ may not represent the occupation number of a real cluster. As explained in the introduction, Mayer clusters are considered to be mathematical rather than physical, but these clusters have many properties which parallel the properties expected of real physical clusters.

By exploiting the properties of the Bell-polynomials (Bell 1934; Riordan 1978), we can express (8) in the following simple and elegant form (Gibbs *et al* 1981),

$$\bar{m}_k = Vb_k(T, V) \frac{Z_{N-k}(T, V)}{Z_N(T, V)}. \quad (9)$$

A comparison of (5) with (9) immediately gives

$$\frac{\bar{m}_1}{N} = \langle e^{-\psi/kT} \rangle^{-1}, \quad (10)$$

where we have used the fact that $b_1 = 1$.

Equation (10) expresses the mean number in terms of the canonical average, $\langle \text{BFT} \rangle$. We shall now use (10) to derive an expression for $\bar{m}_1/N$. We now show that one can easily derive a mean-field approximation to $\langle \text{BFT} \rangle$. In this approximation, one starts by separating the potential into the hard core repulsive and the attractive parts, and one replaces the attractions by a mean-field. If W is the probability that the hard spherical core of the test particle will fit at an arbitrary point without overlapping with the hard cores of any other molecules that are already there, and if ψ_{attr} is the attractive part of the potential felt by the test particle, then we can write

$$\langle e^{-\psi/kT} \rangle = W \langle e^{-\psi_{\text{attr}}/kT} \rangle. \quad (11)$$

The probability W is identified as ρ/z_{HS} , where z_{HS} is the fugacity of the hard sphere fluid at density ρ . We replace the average of the exponential on the right hand side of (11) by the exponential of the average which we denote by ψ_{m_f} ,

$$\psi_{m_f} = \rho \int_{r>\sigma} \phi_{\text{attr}}(r) dr = 2a. \quad (12)$$

$\phi_{\text{attr}}(r)$ is the attractive component of the inter-molecular potential, σ is the diameter of the hard core, and

$$a = -\frac{1}{2} \int_{r>\sigma} \phi_{\text{attr}}(r) dr \quad (13)$$

is van der Waals' parameter a . Combining (11)–(13), we get

$$\langle e^{-\psi/kT} \rangle = \rho/z_{HS} e^{2a\rho/kT}. \quad (14)$$

For hard sphere fluid, the density expansion provides a very good approximation to z_{HS} even at fairly high densities. Formally this is obtained by inverting the well-known (Hill 1956; Mayer and Mayer 1980) fugacity expansion of density

$$\rho(z) = \sum_{l=1} lb_l(T) z^l, \quad (15)$$

which can be inverted to give

$$z_{HS}(\rho) = \rho e^{-F(\rho)}, \quad (16)$$

At very low densities, z and ρ are practically identical, so the function $F(\rho)$ must tend to zero as $\rho \rightarrow 0$. Therefore, it can be expressed as a power series in

$$F(\rho) = \sum_{k=1} \beta_k^{HS} \rho^k. \quad (17)$$

The β_k 's can be identified as star (or irreducible cluster) integrals (Hill 1956; Mayer and Mayer 1980).

By combining (10), (14), (16) and (17) we obtain

$$\frac{\bar{m}_1}{N} = e^{(-2a\rho/kT)} e^{-\sum_{k=1} \beta_k^{HS} \rho^k} \quad (18)$$

For temperatures below the critical temperature, (18) predicts an exponential fall with increasing density at lower densities. This behaviour has been observed in recent numerical calculations (Donoghue and Gibbs 1981).

We can also calculate the occupation number $\bar{m}_k$ for cluster sizes larger than single particle if we make the following approximation

$$\begin{aligned} \frac{Z_{N-k}}{Z_N} &= \frac{Z_{N-1}}{Z_N} \times \frac{Z_{N-2}}{Z_{N-1}} \times \dots \times \frac{Z_{N-k}}{Z_{N-k+1}} \\ &\simeq \left(\frac{Z_{N-1}}{Z_N} \right)^k; \quad k \ll N, \end{aligned} \quad (19)$$

The approximate relation (19) is reasonable for large systems so long as cluster size k is much smaller than total number of particles in the system. In this paper we shall

use (19) to compute $\bar{m}_k$ only for very small values of k . Now, $\bar{m}_k$'s are given by the following expression

$$\frac{\bar{m}_k}{N} \approx b_k \rho^{k-1} \left(\frac{\bar{m}_1}{N} \right)^k. \quad (20)$$

Equation (20) is very much similar to (2), which is the equilibrium solution of the kinetic equation of Becker and Döring (1935) for the time evolution of cluster sizes in nucleation. A closed form expression for the cluster integrals are given by (Mayer and Mayer 1980),

$$b_k = \frac{1}{k^2} \sum_{\{m_l\}} \prod_l \left(k \beta_l \right)^{m_l} / m_l!; \sum l m_l = k-1. \quad (21)$$

Pressure can be expressed as the sum of the mean cluster sizes

$$p/kT = \rho \sum_{k=1} \left(\frac{\bar{m}_k}{N} \right). \quad (22)$$

Next, we present a calculation of the mean number of these cluster sizes for van der Waals' fluid. The reason for choosing van der Waals' fluid is three-fold. First, all of the irreducible cluster integrals are available. Second, an extensive numerical calculation of the mean cluster size distribution for this system has recently been carried out by Donoghue and Gibbs (1981) who used the exact relation (9) to evaluate all the $\bar{m}_k$'s. Their calculation was done numerically and was limited to small system sizes. Third, the mean-field argument is exact for this system.

The star integrals, β_k 's, can be found by expanding the van der Waals' equation of state,

$$\left(p + \frac{N^2 a}{V^2} \right) \left(\frac{V}{N} - b \right) = k_B T. \quad (23)$$

For convenience, dimensional variables are introduced,

$$p^* = \frac{b^2 p}{a}, \quad \rho^* = \frac{Nb}{V}, \quad T^* = \frac{bk_B T}{a}. \quad (24)$$

In this reduced unit

$$\beta_1^{HS} = -2, \quad (25a)$$

$$\beta_{k \geq 2}^{HS} = - \left(\frac{k+1}{k} \right). \quad (25b)$$

One can easily sum the series (17) to obtain

$$F(\rho^*) = -\rho^*/1 - \rho^* + \ln(1 - \rho^*), \quad (26)$$

so that (18) becomes,

$$\frac{\bar{m}_1}{N} (T^*, \rho^*) = (1/1 - \rho^*) \exp(-2\rho^*/T^* + \rho^*/1 - \rho^*). \quad (27)$$

Other $\bar{m}_k$'s are given by (20).

Equation (26) gives the explicit dependence of the fraction of monomers on the temperature and density of the system. This equation should prove useful in the study of nucleation phenomena, especially where the van der Waals' equation provides a good description for the gas phase.

We note that the above mean-field approximation can further be improved if we do a judicious separation of the total potential, e.g. the separation of potential introduced by Weeks, Anderson and Chandler (WCA) (Weeks *et al* 1971). This will lead to an augmented van der Waals' type description (Hansen and McDonald 1976) of the cluster sizes.

3. Results

Figure 1 describes the dependence of m_1/N on the density at three temperatures below the critical point ($T_c^* = 0.296$). At low densities, m_1/N decreases rapidly with increasing density. In the intermediate region, which is bounded by the two spinodal densities, the dependence of $\bar{m}_1/N$ on ρ^* is almost linear. This is in agreement with the numerical calculations of Donoghue and Gibbs (1981) who observed that large clusters appear in the system near the spinodal density. The larger clusters grow in the system as the population of the single particle clusters get depleted.

$\bar{m}_1/N$ shows an increase at still higher densities. We have found that the density at which $\bar{m}_1/N$ again starts to rise is very close to the density at which p^* also starts to rise. However, Mayer's theory with volume independent clusters cannot be trusted near the pure liquid density where very large clusters appear in the system, and Mayer's theory breaks down.

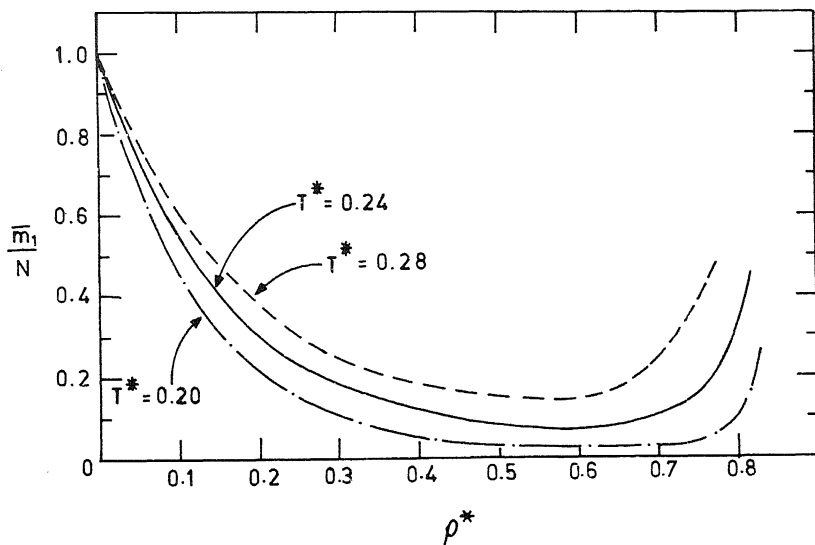


Figure 1. The variation of the number-fraction of monomers ($\bar{m}_1/N$) with the reduced density (ρ^*) at three different temperatures, all below the critical point.

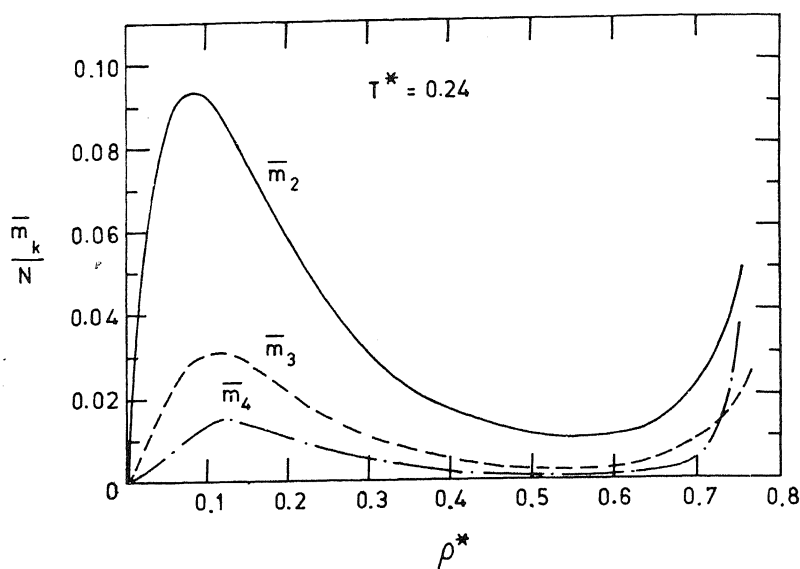


Figure 2. The variation of the number fractions of 2-particle ($\bar{m}_2/N$), 3-particle ($\bar{m}_3/N$), and 4-particle ($\bar{m}_4/N$) clusters with the reduced density at a temperature below the critical point.

Figure 2 describes the variation of the average occupation numbers $\bar{m}_2/N$, $\bar{m}_3/N$ and $\bar{m}_4/N$ with density at a temperature below the critical point. As expected, all of them increase rapidly with density when the density of the system is small. Then they all reach maximum at densities which are little lower than the spinodal density. Beyond the spinodal density, there is a sharp drop in the population of these clusters and they pass through a linear region before they start rising again at a density close to the liquid density.

The sharp decrease in the population of these small clusters near the spinodal density indicates that the population is being shifted to the larger cluster sizes. The sudden appearance of these larger clusters indicates the onset of condensation.

Figure 3 depicts the variation of pressure with density; the pressure is computed from the mean numbers of the first four clusters with the help of (22). We see that the agreement of this pressure with the van der Waals' pressure is very good, even beyond the spinodal density. There is a small loop present in this pressure which is, of course, expected due to the mean-field approximation used in deriving (14) for $\langle \text{BFT} \rangle$. It is rather surprising that so few cluster sizes can give such a good description of the pressure of the system, even beyond the spinodal density.

From figure 1 and from (10), we can learn about the density dependence of $\langle \text{BFT} \rangle$. As density is increased past the spinodal density, $\langle \text{BFT} \rangle$ undergoes a sharp increase indicating the rapid increase of the attractive interactions in the system.

4. Discussion

There are two main results that have come out of the present work. First, we have shown that simple analytic expressions for the average number of small Mayer

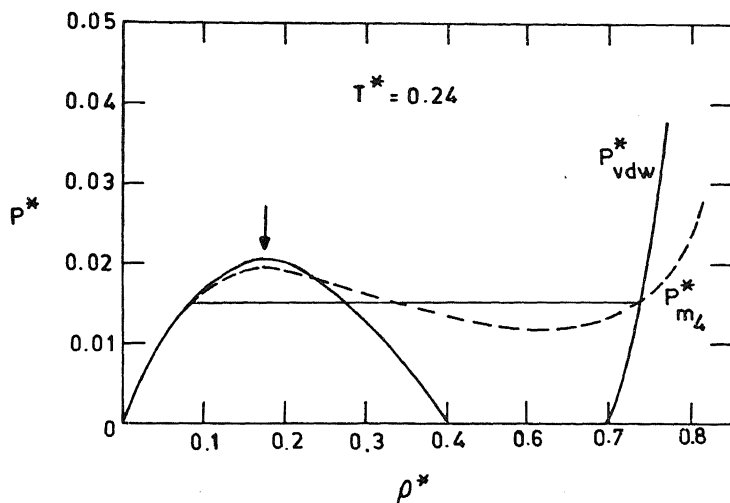


Figure 3. The pressure computed from the average numbers of the first four clusters is plotted against the reduced density (dashed line). Also shown is van der Waals pressure with the Maxwell tie line (solid line). The arrow indicates the first spinodal point.

clusters can be obtained in the mean-field limit. Thus, in order to obtain the population of these small clusters, we do not need to evaluate the full partition function as was done by Gibbs *et al* (1981) and by Donoghue and Gibbs (1981). Second, the main contribution to pressure at densities near the spinodal density arises only from the very small clusters.

The pressure computed from (22) becomes very large at a density ρ_l^* which is given by the solution of the following equation

$$\ln(1 - \rho_l^*) + \frac{\rho_l^*}{1 - \rho_l^*} = \frac{2\rho_l^*}{T^*}. \quad (28)$$

The solution of this equation in fact coincides with the density at which $(\partial p / \partial v)_T$ becomes zero for the second time i.e. at the spinodal point of the superheated van der Waals' liquid. The large liquid like clusters comparable in size to the volume of the system become important at this density and this gives rise to an explosive rise in the value of the pressure.

In conclusion, we want to re-emphasize that the clusters considered in this work are mathematical clusters. However, we have found that these clusters in many respects mimic the behaviour of real physical clusters. We have recently shown (Bagchi 1987) that Mayer's theory breaks down when large mathematical clusters appear in the system which happens near the condensation density. There are, however, some systems for which Mayer clusters do represent the physical reality, Bose-Einstein condensation in ideal Bose gas (Bagchi and Mohanty 1982; Mohanty *et al* 1982). In these cases, the symmetry properties of the wave function of Bose particles give rise to an effective attraction among the particles and large clusters appear precisely at the condensation density (Bagchi and Mohanty 1982; Mohanty *et al* 1982). In these cases, volume dependent cluster integrals are always positive

and since there is no hard-core repulsion, the difference between mathematical and physical clusters do not exist. In the presence of hard core interactions in realistic systems, mathematical and physical clusters may have similar properties at low temperatures ($T < T_c$) where the attractive part of the potential plays important role.

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Studies on interactions of ions with nitromethane and acetonitrile using CNDO/force method

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MS received 2 July 1987; revised 11 September 1987

Abstract. CNDO/force calculations on the complexes of nitromethane and acetonitrile with H^+ , Li^+ , F^- and Cl^- have been carried out to determine their geometrical parameters and stretching force constants. The results are discussed in terms of specific interactions between the ions and the molecules.

Keywords. CNDO/force; geometry optimization; force constants; ion-molecular interactions; nitromethane and acetonitrile.

1. Introduction

Alkaline solutions of nitromethane and interactions of nitromethane with bases are known (Nielson 1969) to exhibit proton transfer leading to the formation of nitronate anions, $[CH_2=NO_2]^-$, whereas the acidic solutions of nitromethane yield nitronic acid, $CH_2=NOOH$. The interactions of nitromethane with metal cations lead to the formation of the salts of nitronic acid. Molecular species exhibiting specific interaction of cations and anions with nitromethane are assumed to be present as intermediates in the formation of the nitronate anion, nitronic acid and the salts of nitronic acid. In such intermediates, the cations interact with the oxygen atom of the $-NO_2$ group and the anions interact with the hydrogen atom of the methyl group. Similarly, in ion-acetonitrile complexes, cations interact with acetonitrile through the lone-pair electrons of the nitrogen atom and anions through the hydrogen atom of the methyl group. While some reports are available in the literature on experimental (Kecki and Wojtzak 1970; Coetzee and Sharpe 1972; Sze 1973; Sastry and Singh 1986) and theoretical (Gabdrakipov and Markina 1979; Sadlej 1979; Curtiss 1979; Yamabe and Hirao 1981) aspects of ion-acetonitrile interactions, no theoretical investigations have been made on ion-nitromethane complexes. Moreover, barring a few attempts on cation-acetonitrile interactions, no systematic studies have been made on the effect of cations and anions on the stretching force constants of these molecules. In this connection we have carried out CNDO/force calculations on several models in which the ions exhibit various types of interactions with nitromethane and

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acetonitrile. The detailed procedures for the optimization of geometries and the calculation of force constants using the CNDO/force method have been reported earlier (Pulay and Torok 1973; Kanakavel *et al* 1976; Annamalai and Singh 1982a, b, c, 1983a, b; Jothi *et al* 1982; Brakaspathy *et al* 1985; Brakaspathy and Singh 1985, 1986a, b), and are not discussed here, for the sake of brevity. Geometry optimization has been carried out for all the models and stretching force constants are calculated. The effect of ion-molecular interactions on their geometrical parameters and stretching force constants are discussed.

2. Results and discussion

2.1 Ion-nitromethane interactions

Two structures for cation interactions and one structure for anion interaction are considered. In structure I of the cation interaction, the cation is assumed to be bonded to one of the oxygen atoms of the nitro group and in structure II the cation is considered to be bonded to both oxygen atoms of the nitro group along the CN axis. Anion interaction is considered through hydrogen-bonding via one of the methyl hydrogen atoms. These interactions are illustrated in figure 1. Geometry optimization for these models have been carried out and their geometrical parameters and stretching force constants are reported in table 1. The force constants were scaled down by suitable scale factors which are derived by comparing the theoretical (CNDO/force) and experimental (refined) force constants of monomer nitromethane (Brakaspathy *et al* 1985). The scale factors employed are 3.64, 4.06 and 2.37, respectively, for CN, NO and CH stretching vibrations. It is noticed that structure I is more stable for $\text{H}^+(\text{CH}_3\text{NO}_2)$ and structure II is more stable for $\text{Li}^+(\text{CH}_3\text{NO}_2)$ complexes. In structure I, the bonded N-O bond length increases from 1.2242 Å to 1.2514 Å on interaction with

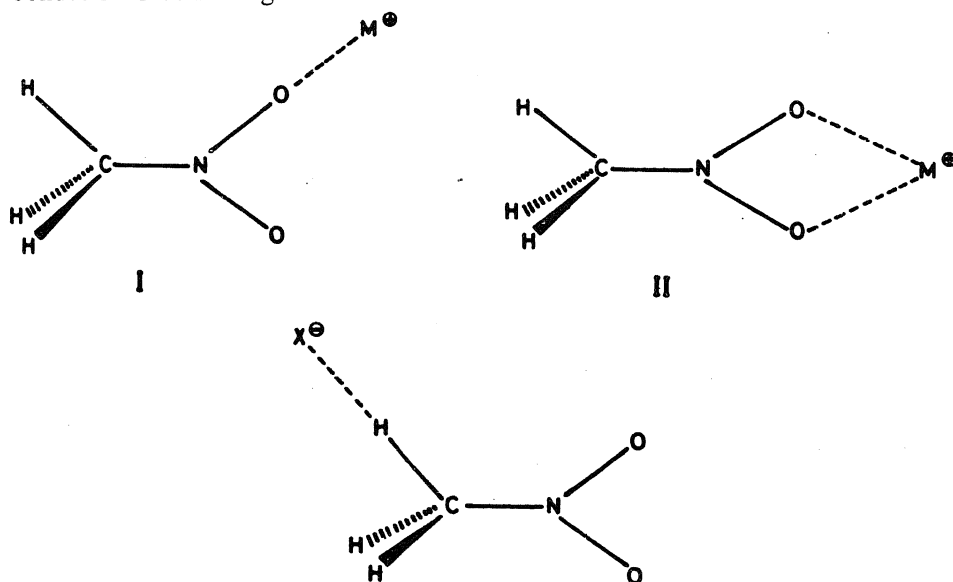


Figure 1. Models for the interaction of cations (I and II) and anion with nitromethane.

Table 1. Geometrical parameters, energies and force constants of ion-molecular complexes of nitromethane^a

Description	H ⁺ (CH ₃ NO ₂)			Li ⁺ (CH ₃ NO ₂)		F ⁻ (CH ₃ NO ₂)	Cl ⁻ (CH ₃ NO ₂)
	Monomer	Model I	Model II	Model I	Model II		
<i>Bond lengths</i>							
CN	1.4173	1.4181	1.3952	1.4158	1.4152	1.4141	1.4155
NO ₁	1.2242	1.2514	1.2204	1.2431	1.2306	1.2260	1.2226
NO ₂	1.2242	1.1992	1.2204	1.2098	1.2306	1.2286	1.2287
CH ₁	1.1170	1.1173	1.1167	1.1182	1.1169	1.3388	1.1498
CH _{2,3}	1.1170	1.1195	1.1206	1.1182	1.1185	1.1219	1.1183
A...ion	—	1.0327	1.2608	2.2679	2.9304	1.1056	1.6959
E _T	-57.94211	-58.35692	-58.34892	-58.03973	-58.05881	-85.56291	-74.08762
<i>Theoretical force constants</i>							
CN	18.14	17.30	19.03	18.10	18.18	17.79	18.19
NO ₁	32.42	31.66	32.56	30.21	30.19	32.97	33.32
NO ₂	32.42	39.70	32.56	36.94	30.19	32.26	31.95
CH ₁	11.95	11.87	11.90	11.83	11.91	5.40	11.01
CH _{2,3}	11.95	11.71	11.63	11.81	11.80	11.42	11.78
A...ion	—	15.54	15.26	1.37	1.14	10.25	3.41
<i>Scaled force constants</i>							
CN	4.98	4.75	5.22	4.97	4.98	4.89	4.99
NO ₁	7.97	7.78	8.00	7.43	7.65	8.11	8.19
NO ₂	7.97	9.76	8.00	9.08	7.65	7.93	7.86
CH ₁	5.05	5.02	5.03	5.00	5.03	2.28	4.65
CH _{2,3}	5.05	4.95	4.91	4.99	4.98	4.83	4.98

^aUnits: bond lengths in Å, total energies, E_T in a.u and force constants in mdyn Å⁻¹

H⁺ whereas its force constant decreases from 7.97 to 7.78 mdyn Å⁻¹. The free N—O bond length decreases to 1.1992 Å whereas its force constant increases to 9.76 mdyn Å⁻¹. Other bonds do not show significant changes. Similar trends are also noticed for Li⁺ interaction. The O—H⁺ and O—Li⁺ distances are found to be 1.0327 Å and 2.2679 Å, respectively. In structure II both the N—O bonds are affected to the same extent. Their force constants change to 8.00 mdyn Å⁻¹ on interaction with H⁺ and 7.65 mdyn Å⁻¹ on interaction with Li⁺.

In the case of anion interaction, it is found that the C—H bond associated with X⁻ is affected to a greater extent than the other bonds. The C—H bond length increases from 1.1170 Å to 1.3388 Å on interaction with F⁻ and 1.1498 Å on interaction with Cl⁻. The corresponding force constants are found to decrease from 5.05 mdyn Å⁻¹ to 2.28 and 4.65 mdyn Å⁻¹ on interaction with F⁻ and Cl⁻, respectively. The greater reduction in the C—H force constant on interaction with F⁻ is justified because of its higher electronegativity and smaller size. The force constants of other bonds are not affected to a significant extent.

2.2 Ion-acetonitrile interactions

The model for cation-acetonitrile interaction is illustrated in figure 2 and the results are tabulated in table 2. It is found that the C≡N force constant decreases from 19.03 mdyn Å⁻¹ to 18.56 mdyn Å⁻¹ on interaction with H⁺. The C≡N force constant is also found to decrease (18.58 mdyn Å⁻¹) on interaction with Li⁺. This

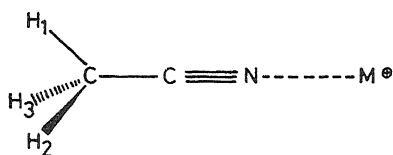


Figure 2. Cation-acetonitrile interaction.

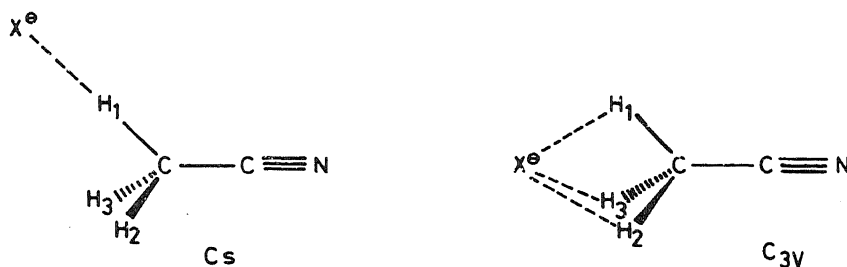
Table 2. Optimized geometries, energies and force constants of cation-acetonitrile complexes^a.

Description	CH ₃ CN	CH ₃ CN...H ⁺	CH ₃ CN...Li ⁺
<i>Bond lengths</i>			
CC	1.4213	1.4015	1.4114
CN	1.1920	1.1993	1.2000
CH	1.1187	1.1203	1.1189
N...M ⁺	—	1.0638	2.0794
E _T	-27.89975	-28.39387	-28.07495
<i>Theoretical force constants</i>			
CC	17.15	17.43	17.61
CN	39.81	38.83	38.87
CH	11.85	11.68	11.78
N...M ⁺	—	14.38	1.98
<i>Scaled force constants</i>			
CC	5.31	5.40	5.45
CN	19.03	18.56	18.58
CH	5.14	5.07	5.11

^aUnits: as given in table 1

is not in agreement with the experimental observations made earlier (Purcell and Drago 1966; Sadlej and Kecki 1969) where C≡N stretching frequency was reported to increase on complex formation.

In the case of anion interactions, two models are considered for X⁻(CH₃CN). In the first model (C_S), X⁻ is bonded to one of the hydrogen atoms of the methyl group and in the second model (C_{3V}), it is symmetrically bonded to all the three hydrogen atoms (figure 3). The geometries and force constants for these species are reported in table 3. The C_S model is predicted to be more stable for F⁻(CH₃CN) whereas C_{3V} model is found to be more stable for Cl⁻(CH₃CN). This is in agreement with the CNDO/2 (Bandura and Novoselov 1978) and *ab initio* (Yamabe and Hirao 1981) results reported earlier. It is found that, in C_S model, the C-H bond length increases from 1.1187 Å to 1.3246 Å on interaction with F⁻ and 1.1512 Å on interaction with Cl⁻. The force constant shows a decrease from 5.14 to 3.32 and 4.52 mdyn Å⁻¹ due to interactions with F⁻ and Cl⁻, respectively. It is experimentally observed in concentrated solutions of lithium bromide in acetonitrile (Sastry and Singh 1986) that a low frequency band appears in the CH-stretching region which is assigned to C-H vibration associated with Br⁻. The frequency shift is of the order of 5 cm⁻¹. Such a low frequency shift may not be surprising as the trend in the stretching force constants for C-H...F⁻ and C-H...Cl⁻ shows that the C-H...Br⁻ force constant may be close to the C-H force constant of the free

Figure 3. Structures of X^- (CH_3CN).Table 3. Optimized geometries, energies, and force constants of X^- (CH_3CN)^a.

		X=F		X=Cl	
Description	Monomer	C _S	C _{3V}	C _S	C _{3V}
<i>Bond lengths</i>					
CC	1.4213	1.3983	1.4346	1.4165	1.4320
CN	1.1920	1.2026	1.1973	1.1939	1.1947
CH ₁	1.1187	1.3246	1.1197	1.1512	1.1241
CH _{2,3}	1.1187	1.1204	1.1197	1.1199	1.1241
A...X	—	1.1241	1.9205	1.7401	2.1985
E _T	-27.89975	-55.49877	-55.41052	-44.03575	-44.04591
<i>Theoretical force constants</i>					
CC	17.15	17.31	14.70	17.42	15.56
CN	39.81	37.42	39.00	39.62	39.39
CH ₁	11.85	7.64	11.44	10.39	11.41
CH _{2,3}	11.85	11.48	11.44	11.68	11.41
A...X ⁻	—	7.46	0.85	2.69	0.45
<i>Scaled force constants</i>					
CC	5.31	5.42	4.55	5.39	4.82
CN	19.03	17.89	18.64	18.94	18.83
CH ₁	5.14	3.32	4.97	4.52	4.95
CH _{2,3}	5.14	4.98	4.97	5.07	4.95

^aUnits: as given in table 1

acetonitrile. The C—C force constant is found to increase from 5.31 to 5.42 and 5.39 $\text{mdyn } \text{\AA}^{-1}$ on interaction with F^- and Cl^- , respectively, whereas the $\text{C}\equiv\text{N}$ force constant is found to decrease from 19.03 to 17.89 and 18.94 $\text{mdyn } \text{\AA}^{-1}$ due to these interactions. The ion-molecular distances are found to be 1.1241 $\text{\AA}$ and 1.7401 $\text{\AA}$ respectively for $\text{F}^-(\text{CH}_3\text{CN})$ and $\text{Cl}^-(\text{CH}_3\text{CN})$ complexes.

The effect of anion interactions on the C—H stretching force constant is found to be small in the C_{3v} model. The C—H force constant decreases from 5.14 to 4.97 and 4.95 $\text{mdyn } \text{\AA}^{-1}$ on interaction with F^- and Cl^- , respectively. The C—C stretching force constant decreases from 5.31 to 4.55 $\text{mdyn } \text{\AA}^{-1}$ on interaction with F^- and it decreases to 4.82 $\text{mdyn } \text{\AA}^{-1}$ on interaction with Cl^- . The $\text{C}\equiv\text{N}$ force constant also decreases from 19.03 to 18.64 and 18.83 $\text{mdyn } \text{\AA}^{-1}$ on interactions with F^- and Cl^- respectively. The ion-molecular distances are found to be 1.9205 $\text{\AA}$ and 2.1985 $\text{\AA}$ for F^- and Cl^- interactions, respectively.

Two hydrogen-bonded structures, namely non-linear (I) and linear (II) are considered for $X^- (\text{CH}_3\text{CN})_2$ complexes. In the non-linear structure, X^- is bonded to one of the hydrogen atoms of the methyl group and in the linear structure it is bonded to all the three hydrogen atoms of the methyl group (figure 4). The geometrical parameters, energies and force constants for these models are given in table 4. It is found that the non-linear model is more stable for $\text{F}^- (\text{CH}_3\text{CN})_2$ and the linear model for $\text{Cl}^- (\text{CH}_3\text{CN})_2$. This is in accordance with the results reported earlier (Yamabe and Hirao 1981). The C-H force constant for the non-linear model decreases from 5.14 to 4.18 mdyne $\text{\AA}^{-1}$ on interaction with F^- and it decreases to 4.73 mdyne $\text{\AA}^{-1}$ on interaction with Cl^- . The decrease in the C-H force constant for the linear model is not as significant as that of the non-linear model. In the linear model the corresponding C-H stretching force constant values are found to be 4.93 and 4.96 mdyne $\text{\AA}^{-1}$ respectively. The reduction in the C-H force constant is found to be less for disolvates than for monosolvates. It is observed that the C-C stretching force constant increases in the non-linear model whereas it is found to decrease in the linear model. In the non-linear model the C-C stretching force constant increases from 5.31 to 5.72 and 5.39 mdyne $\text{\AA}^{-1}$ on interactions with F^- and Cl^- whereas it decreases to 4.62 mdyne $\text{\AA}^{-1}$ and 4.79 mdyne $\text{\AA}^{-1}$ on F^- and Cl^- interactions, respectively. The same trend is observed for monosolvates also. The $\text{C}\equiv\text{N}$ force constant is also found to decrease in disolvates, the change being almost the same for both the models.

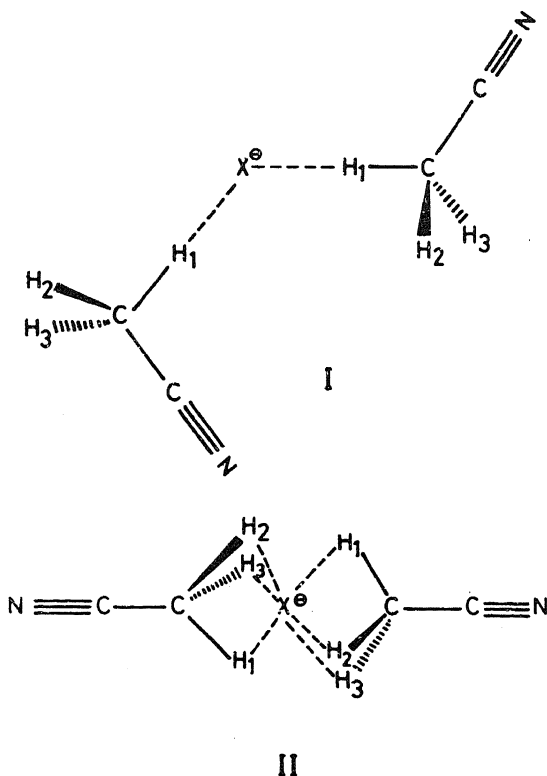


Figure 4. Structures of $X^- (\text{CH}_3\text{CN})_2$: non-linear (I) and linear (II).

Table 4. Optimized geometries, energies, and force constants for X^- (CH_3CN)^a.

Description	Monomer	X=F		X=Cl	
		Model <u>I</u>	Model <u>II</u>	Model <u>I</u>	Model <u>II</u>
<i>Bond lengths</i>					
CC	1.4213	1.4101	1.4425	1.4173	1.4339
CN	1.1920	1.1970	1.1973	1.1939	1.1954
CH ₁	1.1187	1.2096	1.1221	1.1196	1.2278
CH _{2,3}	1.1187	1.1195	1.1221	1.1196	1.2278
A...X ⁻	—	1.2554	1.9365	1.7716	2.1391
E _T	-27.89975	-83.42397	-83.33806	-71.96191	-72.98459
<i>Theoretical force constants</i>					
CC	17.15	18.47	14.92	17.40	15.45
CN	39.81	39.49	49.14	39.27	39.27
CH ₁	11.85	9.62	11.36	10.89	11.44
CH _{2,3}	11.85	11.62	11.36	11.67	11.44
A...X ⁻	—	5.16	1.02	2.43	1.09
<i>Scaled force constants</i>					
CC	5.31	5.72	4.62	5.39	4.79
CN	19.03	18.88	18.71	18.77	18.77
CH ₁	5.14	4.18	4.93	4.73	4.96
CH _{2,3}	5.14	5.04	4.93	5.04	4.96

^aUnits: as given in table 1

3. Conclusions

It is observed from the computed values given in table 1 that the interactions of H^+ and Li^+ with one of the N—O bonds (model I) of the nitromethane reduces the force constant of the associated N—O bond whereas it increases considerably the force constant of the unassociated N—O bond. These values suggest that the cation-nitromethane complexes may produce species of the type $[-\text{N} \leq \overset{\text{O}}{\underset{\text{M}}{\text{O}}}]^{\oplus}$ on such interactions, thus resulting in the increase in the double bond character of one of the N—O bonds and decrease of that of the other. The theoretical force constant for $\text{O}—\text{H}^+$ and its bond length reveal that the bond between the oxygen atom of the NO_2 group and the H^+ ion is almost covalent in character. Interaction of H^+ through both N—O bonds (structure II) does not reduce the force constant whereas Li^+ reduces the force constants of both N—O bonds equally. The C—H force constant is found to decrease on interaction with halide ions, whereas the C—N and N—O force constants do not show significant changes.

The decrease in the $\text{C} \equiv \text{N}$ stretching force constant of acetonitrile on interaction with cations is contrary to the observations made earlier (Purcell and Drago 1966; Sadlej and Kecki 1969). This may be explained on the basis of the fact that the lone-pair orbitals have contributions from anti-bonding π -orbitals, and the bonding of the $\text{C} \equiv \text{N}$ group through its lone-pair electrons with cations would lead to the stabilization of these moieties which would eventually increase the $\text{C} \equiv \text{N}$ stretching force constant. This effect may be reflected in the calculations provided that the anti-bonding π -orbital character is incorporated in the lone-pair orbitals of the oxygen atom through configurational interaction which has not been attempted in the present studies. The interaction of anions with the $-\text{CH}_3$ groups of

nitromethane and acetonitrile reduces the C-H stretching force constant; the reduction being greater in nitromethane than in acetonitrile. This is probably because the NO_2 group is more electron-withdrawing than $\text{C}\equiv\text{N}$ thus making the C-H bond of nitromethane more acidic than that in acetonitrile. This is evident from the higher value of the force constant for $\text{H}^+\text{---F}^-$ in the case of nitromethane than in the case of acetonitrile. It is also observed in the Raman spectra of solutions of acetonitrile that a new band appears in the low frequency region of the C-H stretching mode when the concentration of bromide ion is increased. The $\text{O}^+\text{---H}^+$ and $\text{N}^+\text{---H}^+$ force constants for $\text{H}^+(\text{CH}_3\text{NO}_2)$ and $\text{H}^+(\text{CH}_3\text{CN})$ are in the range of their covalent force constant values. These computed values give an indication that proton transfer takes place in these systems. The theoretical force constants for $\text{O}^+\text{---Li}^+$ and $\text{N}^+\text{---Li}^+$ ranges between 1.40 and 2.00 mdyn $\text{\AA}^{-1}$. The $\text{H}^+\text{---Cl}^-$ force constant is found to have values between 5 and 10 mdyn $\text{\AA}^{-1}$. These theoretical values are unscaled, and with the usual scaling factors ranging between 2 and 3, true values for the above bonds may be estimated. The trends in the theoretical stretching force constants for systems exhibiting ion-molecular interactions have been compared with the experimental vibrational frequencies. However, it may be noted that the values obtained theoretically are for isolated systems in vacuum whereas those obtained experimentally are for condensed systems.

Acknowledgement

The authors acknowledge the financial grant from the Department of Science and Technology, Government of India.

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One-electron reduction of thionine studied by pulse radiolysis

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MS received 25 May 1987; revised 26 August 1987

Abstract. One-electron reduction of thionine has been studied by using the technique of nanosecond pulse radiolysis and kinetic spectrophotometry. H , e_{aq}^- as well as radicals derived from methanol, ethanol, isopropanol, THF, dioxane and *t*-butanol by H atom abstraction were used as reductants. The rate constants for the transfer of electrons from these radicals to thionine were directly determined from the pseudo first-order formation rates of the product, semithionine and the one-electron reduction potential of thionine estimated. The absorption spectrum of semithionine in its different conjugate acid-base forms was found to be in agreement with previously reported spectra and the decay of the species was second order. By monitoring transient absorbance changes as a function of pH, two pK_a values were observed and, based on the effect of ionic strength on the second-order decay constants of the species were assigned to the equilibria described.

Keywords. One-electron reduction of thionine; pulse radiolysis; kinetic spectrophotometry; semithionine; thionine.

1. Introduction

Thionine and other thiazine dyes have been used in photogalvanic cells to convert light to electrical energy (Rabinowitch 1940; Kamat *et al* 1979). Because of this, many studies have been reported in the past concerning its photoreduction by ferrous ions and other reducing agents, both by steady-state and flash-photolytic techniques (Ainsworth 1960; Hatchard and Parker 1961; Fischer *et al* 1970; Bonneau and Pereyre 1975; Guha *et al* 1979). The intermediate product of photoreduction has been identified as the short-lived species semithionine, which in certain pH ranges and in surfactant-free solutions has been shown to form a complex with Fe^{2+} ions (Guha *et al* 1985). In order to study the spectra and kinetics of formation of this species in aqueous solutions in the absence of complex forming ions, we have employed the technique of pulse radiolysis and kinetic spectrometry (Hunt and Thomas 1967). In this technique, a dilute aqueous solution containing the compound to be studied is subjected to a short duration (a few nanoseconds) burst of energetic electrons which by primary interaction with the solvent water generate strongly reducing species, viz. hydrated electrons (e_{aq}^-) and hydrogen atoms (H), and oxidizing species, viz. hydroxyl radicals (OH). By the choice of suitable reagents (see §2) it is possible to investigate exclusively the reactions of the reducing or oxidizing species. We have studied aqueous solutions of thionine under the former conditions and the results of this study are reported here.

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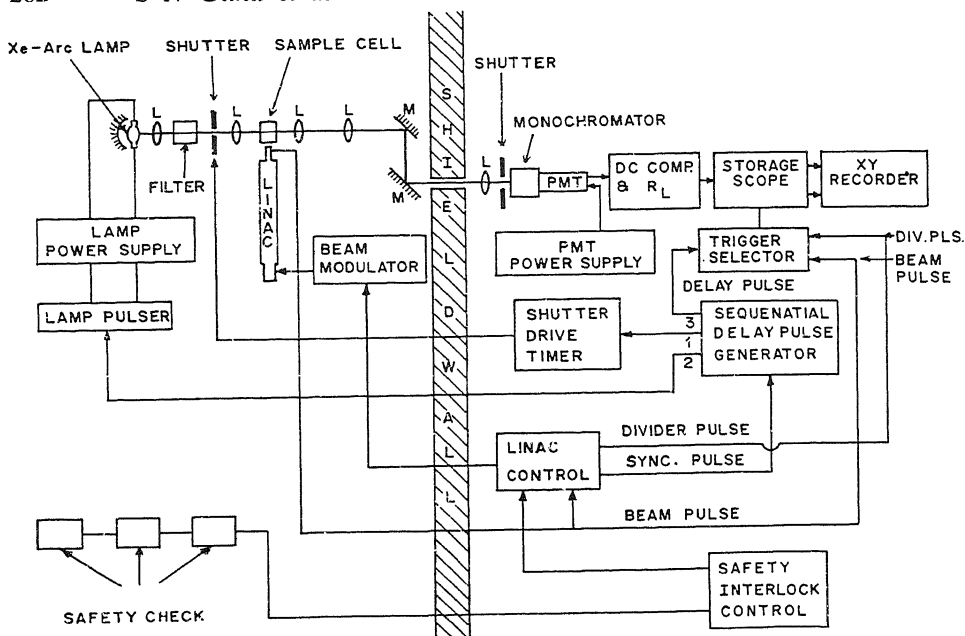


Figure 1. Schematic diagram of pulse radiolysis set-up.

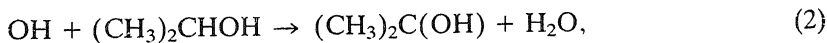
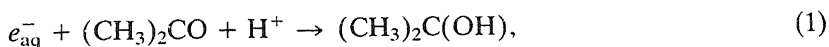
2. Experimental

The pulse radiolysis apparatus is shown schematically in figure 1. It consists of an electron linear accelerator (Viritech Ltd., England) capable of giving single shots of 5–25 ns, 7 MeV electron pulses at peak current of ~ 1 A. The pulse irradiates the sample contained in a $1\text{ cm} \times 1\text{ cm}$ 'Suprasil' square cuvette kept at a distance of ~ 12 cm. from the electron beam window, where the beam diameter is ~ 1 cm. The transient changes in the absorbance of the solution caused by the electron beam pulse are monitored with the help of a collimated light beam from either a steady 250 Watts tungsten halogen lamp (for slow signals) or a pulsed 450 W Xenon arc lamp (for fast signals). The accelerator, sample cell and monitoring light source are housed in a shielded cave and the monitoring light beam, after passing through the sample cell is directed to the detection room through a tunnel in the shield wall* with the help of fused silica lenses and front aluminium coated mirrors. The light beam is finally focussed on to the entrance slit of a grating monochromator (Kratos Analytical Instruments Inc., USA, model GMA-252) over the exit slit of which is fixed a photomultiplier tube (PMT-Hamamatsu TV Co., Japan, Model R-955) with uniform spectral response in the region 185–900 nm. The voltage to the PMT is supplied from a high voltage power supply (Electronics Corporation of India, Model HV 4800 D). The PMT voltage divider network is similar to the one described by Hunt and Thomas (1967) for nanosecond response. The output signal from the PMT is fed through a manual DC offset circuit to the Y input of a 100 MHz storage scope (Iwatsu Electric Co., Japan, Model TS 8123). An electrically operated shutter (Vincent Associates, USA, Model 225-L) interposed

* 1.5 m thick concrete.

between the monitoring light source and the sample cell is normally kept closed to prevent the photolysis of the sample and can be opened for a duration of ~ 50 ms covering the electron beam pulse period. Within this time period, the intensity of the Xenon arc lamp light output is increased 20–100 times for a duration of ~ 5 ms to achieve improved S/N ratio. Synchronisation of the electron beam pulse with the shutter opening, pulsing of the arc lamp and triggering of the base line of the storage scope is accomplished with an indigenously developed sequential delay pulse generator. Appropriate cut-off filters are interposed before the monochromator entrance slit to eliminate artifacts from second-order diffracted light of shorter wavelengths.

Thionine used was Fluka 'Puriss' grade and was further purified as described by Guha *et al* (1982). Other chemicals were all BDH 'Analar', S Merck 'GR' or J T Baker 'Analysed' grade and were used without further purification. Solutions were prepared in triply distilled water. For pH adjustments H_2SO_4 , Na_2HPO_4 , KH_2PO_4 , $Na_2B_4O_7 \cdot 10H_2O$ and $NaOH$ were used in suitable combinations, keeping the total ionic strength equivalent to that of ~ 0.04 mol dm^{-3} 1:1 electrolyte. Indian Oxygen Ltd. 'IOLAR' grade N_2 and Matheson 'Research' grade N_2O were used for purging of solutions. For measuring the electron pulse dose, 0.05 mol dm^{-3} aerated KCNS solution was used, taking $G\epsilon$, for the $(CNS)_2^-$ species generated in this system, to be 21522 dm³mol⁻¹cm⁻¹ per 100 ev at 500 nm (Fielden 1984). Doses generally used were 1.5×10^{17} eV cm⁻³ per pulse. For extinction coefficient measurements a lower dose (1/5 th of the above) was employed. For studying reactions of e_{aq}^- at pH 6, the solutions contained 0.1 mol dm^{-3} *t*-butanol to scavenge OH radicals, the reaction products of which were first shown to be unreactive towards thionine. Reactions of H atoms were studied in acidic solutions (pH ~ 3) where the e_{aq}^- are quantitatively converted to H by reaction with H^+ ions within the electron pulse duration; 0.1 mol dm^{-3} *t*-butanol served as OH scavenger. A matrix containing 1.0 mol dm^{-3} isopropanol and 0.1 mol dm^{-3} acetone served to convert all of e_{aq}^- , H and OH to reducing $(CH_3)_2C(OH)$ radicals over the entire pH range from ~ 0.1 to 13. This is possible because at pH 5 where H^+ concentration is too low to convert e_{aq}^- to H and then to $(CH_3)_2C(OH)$, acetone reacts with e_{aq}^- to give the same species within the electron pulse duration:

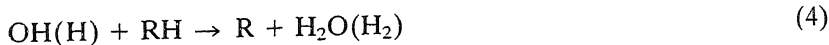


$$(k_1 = 5.9 \times 10^9 \text{ and } k_2 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}).$$

Radicals of other organic compounds (viz. ethanol, methanol, glucose, dioxane and tetrahydro furan) were generated in N_2O saturated solutions at pH 6 via reactions 3 and 4.



$$(k_3 = 8.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}),$$



$$(k_4 = 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for the compounds used}).$$

In calculating the extinction coefficients of the semithionine species produced by pulse radiolytic reduction, the fraction of H atoms reacting with thionine by processes other than electron transfer was taken as 11% (Solar *et al* 1982). Corrections were also made to account for the fraction of e_{aq}^- , H and other radicals being lost by mutual reaction, and for the percentage of non-reducing $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ radicals formed in (4) in the acetone-isopropanol system. G-values for e_{aq}^- , H and OH as reported by Draganic and Draganic (1971) were used.

3. Results and discussion

The well-known absorption band of the hydrated electron with λ_{max} at 720 nm (Keene 1964), which decays predominantly by second-order kinetics in an electron beam pulsed deoxygenated $10^{-1} \text{ mol dm}^{-3}$ *t*-butanol matrix (pH 9.6), was found to decay much faster and by first-order kinetics in the presence of thionine, the rate constant depending on thionine concentration, thus indicating the high reactivity of this compound with e_{aq}^- . The bimolecular rate constant for this reaction evaluated from such pseudo first-order decay traces was $2.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. On monitoring transient absorbance over the entire spectral region barring that covering the absorption bands of thionine itself, a well-defined spectrum with absorption maximum at 400 nm was observed. Typical signals showing the disappearance of e_{aq}^- at 720 nm and formation of product species at 400 nm are given in figure 2. The build-up of absorbance after the electron pulse at this wavelength occurred over the same time period as the decay of the hydrated electron and was pseudo first order with respect to thionine concentration. The bimolecular rate constant ($k_{e_{aq}^-} + \text{thionine}$) evaluated from such build-up traces was $3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is $\sim 15\%$ higher than the one obtained by following e_{aq}^- decay because of the error introduced by the subsequent decay of the species. However, even the latter value is much higher (nearly twice) than the

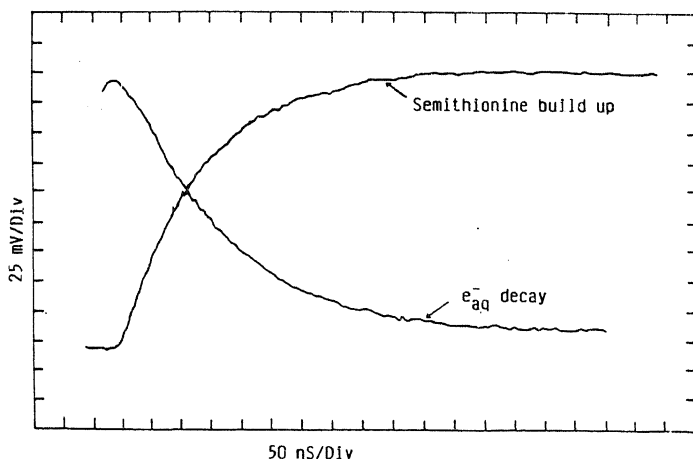
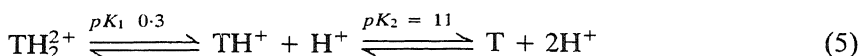


Figure 2. Decay of hydrated electron absorption (720 nm) and build up of semithionine absorption (400 nm) in aqueous solution at pH 9.6 (0.1 mol dm^{-3} *t*-butanol, $2 \times 10^{-4} \text{ mol dm}^{-3}$ TH^+ , O_2 -free system).

values reported for the rate constant of this reaction by Solar *et al* (1982): 1.1 and $1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, at pH 7.6 and 12.6. The presence of impurities in the thionine employed could be causing the lower values, for we found that unpurified thionine gave $1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for this rate constant at pH 7.6. It is also to be noted that thionine itself is rather unstable in highly alkaline solutions. Its pK_a values are ~ 0.3 and 11 (Kramer and Maute 1972), the conjugate acid-base forms involved being:



Because of its instability in the highly alkaline medium, the reactivity of the fully deprotonated form (T) could not be determined. But at pH 11 where both TH^+ and T forms are present in equimolar concentrations the observed rate constant was, within limits of experimental error, the same as that at pH 9.6 where thionine is predominantly present in the TH^+ form. It is therefore to be inferred that the two forms TH^+ and T have almost identical reactivity with e_{aq}^- . Further the disappearance of the hydrated electron (monitored at 720 nm) and formation of a transient species absorbing at 400 nm are both due to the same process, viz., the one-electron reduction of thionine by e_{aq}^- , and therefore the species absorbing at 400 nm must be the one-electron reduction product, semithionine. This inference is supported by the observation that the transient absorption at 400 nm was absent if an oxygen-saturated solution was pulsed under otherwise identical conditions. O_2 has a very high reactivity towards e_{aq}^- ($k_{e_{\text{aq}}^- + \text{O}_2} = 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and in an oxygen-saturated solution where $[\text{O}_2] \approx 10^{-3} \text{ mol dm}^{-3}$, the e_{aq}^- reacts exclusively with O_2 and not with the thionine present at a concentration of $< 10^{-4} \text{ mol dm}^{-3}$. This observation also shows that O_2^- the product of e_{aq}^- scavenging by O_2 is not capable of reducing thionine.

The complete absorption spectrum of the transient species at this pH (figure 3a) was recorded in electron beam pulsed oxygen-free $8 \times 10^{-5} \text{ mol dm}^{-3}$ thionine solution containing 1.0 mol dm^{-3} isopropanol and 0.1 mol dm^{-3} acetone. A well-defined absorption band with λ_{max} at 400 nm and another merging into the thionine absorption band at 630 nm were observed. The absorbances at these wavelengths were found to build up to a maximum at $\sim 3 \mu\text{s}$ after the electron pulse, and decayed by second-order kinetics on a time scale similar to the 400 nm absorption in the *t*-butanol matrix referred to earlier. From this it is inferred that the species formed in the two matrices are the same. Further, for the same dose, the absorbance in the isopropanol acetone matrix where the e_{aq}^- , H and OH are almost quantitatively converted to the reducing $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals, and $G (= 5.95)$, was almost double that found in the *t*-butanol matrix $G_{e_{\text{aq}}^-} (= 2.63)$. These observations suggest that thionine undergoes one-electron reduction by $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals to give semithionine. As expected on this basis, in O_2 -saturated solutions where the $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals are converted to the non-reducing peroxy radicals, the transient spectrum of semithionine was not observed on electron beam pulsing. At lower pH values the 630 nm band was appreciably red-shifted (to 770 nm). Monitoring absorbance changes at 770 nm as a function of pH in electron beam pulsed oxygen-free 1 mol dm^{-3} isopropanol, 0.1 mol dm^{-3} acetone matrix containing $5 \times 10^{-5} \text{ mol dm}^{-3}$ thionine revealed two inflexion points at pH 1.8 and 8.1 (figure 4). Therefore, three conjugate acid-base

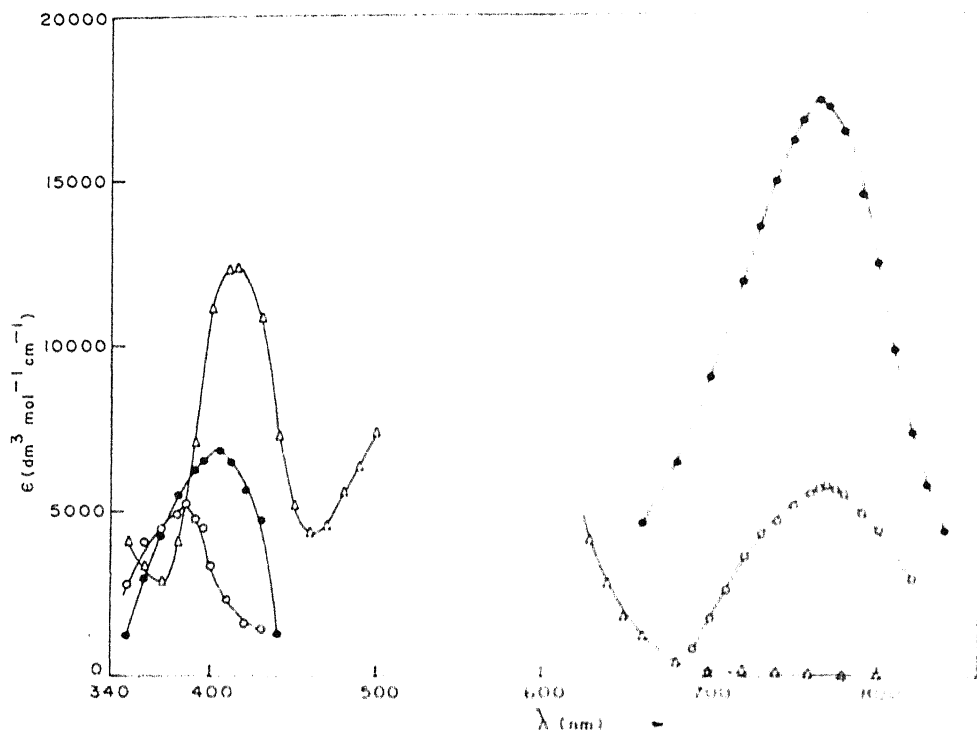
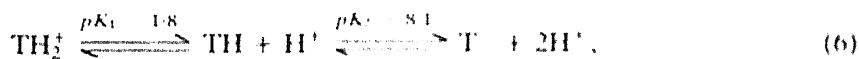


Figure 3. Absorption spectrum of transient semithionine species in a pulse irradiated aqueous solutions: pH 0.25 (Δ), 6 ($\bullet$) and 9.6 ($\circ$).

forms of semithionine are indicated. If we represent the neutral thionine molecule as T, the above equilibria for the one-electron reduction product semithionine could be one of the following.



or



The spectra of the three forms as monitored at $\sim 3 \mu\text{s}$ after the electron pulse in matrices of 1 mol dm^{-3} isopropanol and 0.1 mol dm^{-3} acetone, pH 0.25, 6.0 and 9.6 are given in figure 3, and values of λ_{max} and ϵ_{max} of semithionine at these pH values are given in table 1. It may be noted that these spectra agree with those reported by Solar *et al* (1982); however, our detection system was not sensitive enough to enable us to observe the peaks in the region $\lambda < 300 \text{ nm}$. Also the gap in the region of $\lambda \sim 480\text{--}620 \text{ nm}$ is due to strong absorption by thionine itself. It is seen that all the forms are characterized by a band in the 400 nm region with small shifts in the λ_{max} . The other band in the longer wavelength region has λ_{max} around 770 nm at pH values 0.25 and 6.0 but at 9.6 it is appreciably blue-shifted and merges with the absorption band of thionine itself. The spectrum at pH 13 was

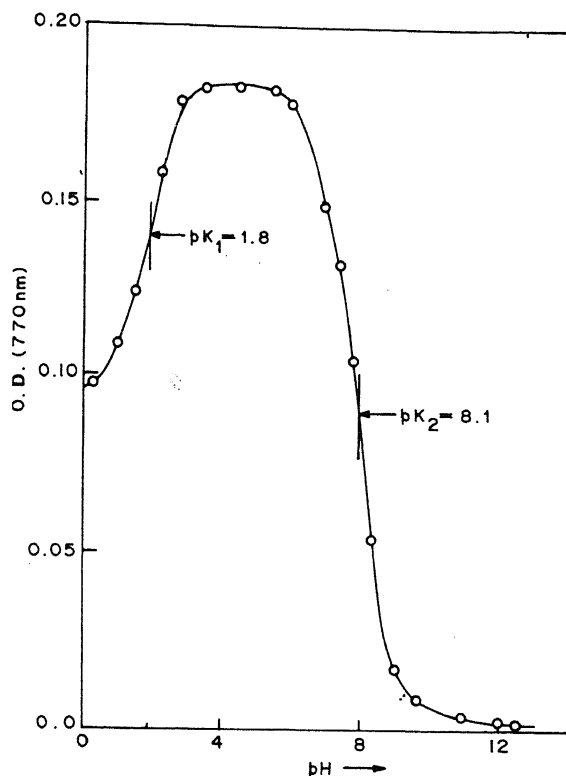


Figure 4. pK of semithionine species.

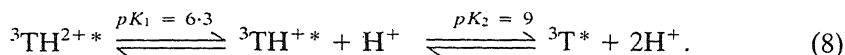
Table 1. Absorption maxima, extinction coefficients and decay kinetics of the semithionine radical.

pH	Protonated form of semithionine	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$2k$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)*	
				No added salt	In the presence of added salt
0.25	TH_3^{2+}	$\begin{cases} 385 \\ 770 \end{cases}$	$\begin{cases} 5,220 \\ 5,785 \end{cases}$	2.1×10^9	—
6.0	TH_2^+	$\begin{cases} 400 \\ 770 \end{cases}$	$\begin{cases} 6,826 \\ 17,200 \end{cases}$	2.1×10^9	3.0×10^9 (0.1M Na_2SO_4) 3.5×10^9 (0.1M NaClO_4)
9.6	TH	$\begin{cases} 400 \\ 630 \end{cases}$	$\begin{cases} 12,380 \\ — \end{cases}$	1.8×10^9	1.8×10^9 (0.1M Na_2SO_4)

* Second-order rate constant for the dismutation of semithionine

identical to the one at pH 9.6, except that the longer wavelength band was better defined, as at this pH the corresponding spectral band of thionine is also appreciably blue-shifted and hence does not interfere with that of the product species; hence a clear maximum at 630 nm was evident.

In order to distinguish between the two protolytic equilibria, (6) and (7), for semithionine, the effect of ionic strength on the second-order decay constant of the species present at pH 9.6 and 6 was investigated. The results (table 1) clearly indicate that the species at pH 9.6 is neutral whereas the one at pH 6 is charged. The increase in rate constant at high ionic strength at pH 6 is close to that expected for reaction between two singly-charged species. Hence the scheme represented by (7) must be correct. A similar conclusion has been arrived at by Bonneau *et al* (1968) in their work on the flash-photolytic reduction of thionine using phenylene diamine as photoreductant. In this connection it may be noted that although Solar *et al* (1982) have reported $pK_1 = 1.8$ for semithionine they have not reported the second pK value. An earlier report (Kramer and Maute 1972) of $pK_2 = 8.1$ for this species as due to the equilibrium between TH_2^+ and TH forms was based on photoreduction of thionine in the presence of organic reducing agents. In such experiments the initially formed thionine triplet which has two pK values (Kramer and Maute 1972) corresponding to the equilibria:



accepts an electron from the organic compound to give semithionine. Inference of a $pK_2 = 8.1$ for the product semithionine from such experiments is somewhat ambiguous in view of the two pK values of the thionine triplet in close proximity; also the organic reductant used, viz. EDTA, has pK values in the same region further complicating the interpretation. On the other hand, the observation of pK_1 and pK_2 in the present pulse radiolysis experiments is not subject to such limitations as the reducing species $(CH_3)_2COH$ used has a $pK = 12$ (Moorthy and Hayon 1974). Besides, the assignment of the different conjugate acid base forms of semithionine on the basis of ionic strength effect on the second-order decay constants of these different forms is also unambiguous.

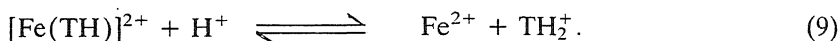
3.1 Reaction with H-atoms

In the oxygen-free 0.1 mol dm^{-3} *t*-butanol matrix at pH ~ 3 where the e_{aq}^- are quantitatively converted to H atoms by reaction with H^+ ions and the OH radicals are scavenged by *t*-butanol, the transient species formed by reaction of H atoms was found to be identical to the one produced by reduction with $(CH_3)_2C(OH)$ radicals at the same pH with respect to both λ_{max} and decay kinetics. This suggests that the H atom preferentially acts as a one-electron reductant rather than add on to the heteroaromatic ring of thionine. By computer analysis of their pulse radiolysis data Solar *et al* (1982) have indirectly inferred that only about 11% of H atoms add on to the ring and the rest bring about reduction of thionine to semithionine. From the pseudo first order rate constant for build-up of transient semithionine at 770 nm in the oxygen free 0.1 mol dm^{-3} *t*-butanol matrix (pH ~ 3)

containing different concentrations of thionine we have deduced the bimolecular rate constant for its reaction with H atoms to be $9.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which may be compared with the value of $8.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ reported by Solar *et al* (1982). Again our value is higher than the latter for the same reason as discussed for the e_{aq}^- reaction rate constant.

3.2 Comparison with the results of photoreduction studies

In our earlier studies on the photoreduction of thionine by ferrous ions (Guha *et al* 1979, 1985) it was observed that the spectrum of the product transient semithionine species was characterised by a fine structure in the longer wavelength band. This fine structure became predominant at high Fe^{2+} concentration and at higher pH, say 3.5 and was attributed to the complexed semithionine species and an equilibrium of the type:



In the present study, where the system does not contain Fe^{2+} ions, it is significant that the spectra are devoid of fine structure, thus indirectly supporting the earlier conclusions.

3.3 Reactions of thionine with other reducing radicals

H and OH radicals formed in electron pulsed aqueous solutions react very fast with organic molecules such as ethanol, methanol, glucose, dioxane and tetrahydrofuran by hydrogen abstraction (4) to give radicals which are reducing in nature as in the case of $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals from isopropanol. In N_2O saturated neutral aqueous solutions where e_{aq}^- are quantitatively converted to OH, the electron beam pulsed aqueous solutions of these compounds contain only the above reducing radicals. In order to determine their effectiveness as one-electron reducing agents N_2O saturated, neutral 0.1 mol dm^{-3} solutions of these compounds containing $10^{-4} \text{ mol dm}^{-3}$ thionine were subjected to the same dose of 25 ns electron pulses and the maximum transient absorbances reached $\sim 10 \mu\text{s}$ after the pulse were determined. The transient spectra obtained were identical to the ones observed in similar isopropanol matrices. From the transient build-up traces the rate constants for the corresponding one-electron reductions were evaluated. The results, along with those for isopropanol, are given in table 2 and figure 5. It is seen that the reducing efficiency of these radicals more or less follows the trend in their known one-electron reduction potentials. From the inflexion point of the curves in figure 5 the one-electron reduction potential of thionine is inferred to be $+0.05\text{V}$ (vs NHE). This value therefore explains the ability of thionine to undergo easy one-electron reduction by H atoms. In the past, indirect estimate of the one-electron reduction potential of thionine had been made (Rabinowitch 1940), the value at pH 2 ranging from 0.25 to 0.35 V. Taking into consideration the involvement of a proton in the reduction step:



the above value leads to -0.045 to $+0.055 \text{ V}$ for the reduction potential at pH 7.

Table 2. Rate constant for the one-electron reduction of thionine by organic radicals (pH 6.8).

Organic radical derived from	$*E^{\circ 1}$ (vs. NHE) (neutral pH)	$k_{II}^{\dagger}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
1. Isopropanol	-1.05	4.6×10^9
2. EtOH	-0.95	4.9×10^9
3. MeOH	-0.73	4.6×10^9
4. THF	-0.55	4.6×10^9
5. Dioxane	+0.05	2.7×10^9
6. Glucose	+0.06**	1.6×10^9
7. <i>t</i> -Butanol	+0.15	0.0
8. Cytosine	-0.12 [†]	4.2×10^9

[†] Bimolecular rate constant; * Lilie *et al* (1971); Henglein (1976);

** This value is for ribose radicals (Rao and Hayon 1974); [†] Rao and Hayon (1974)

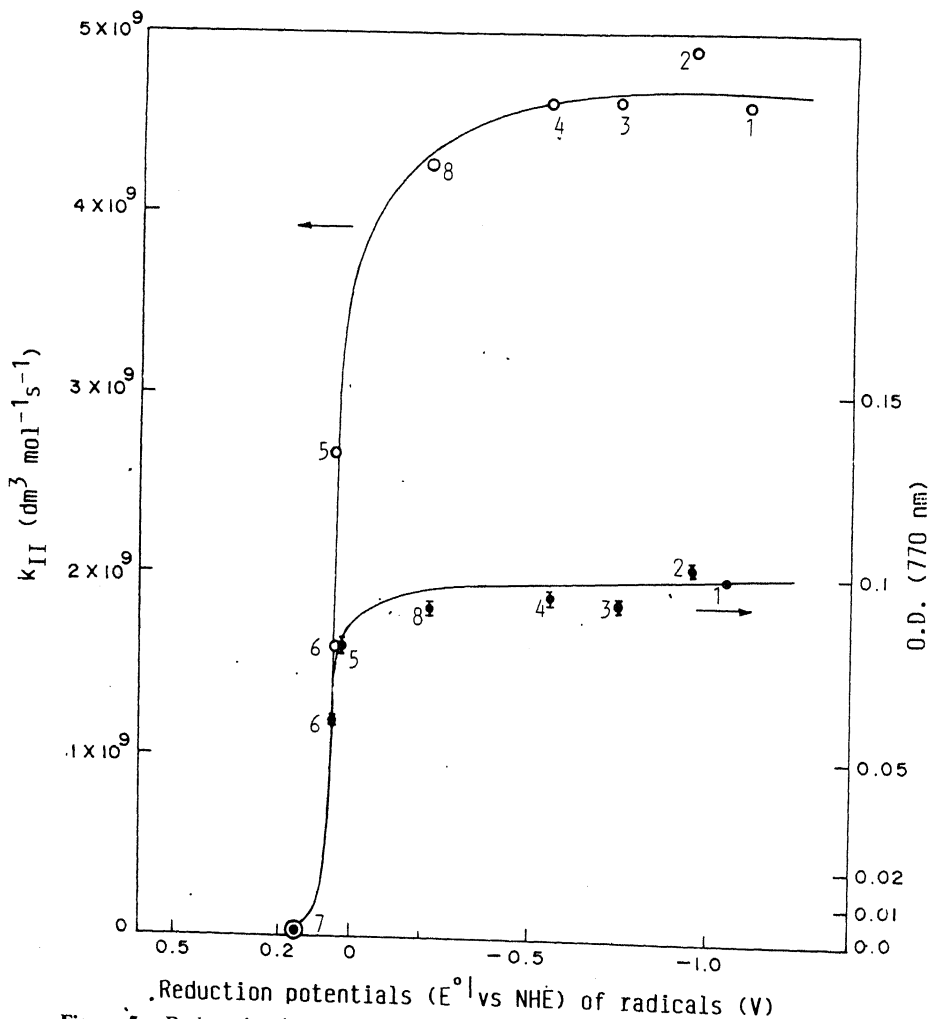


Figure 5. Redox titration curve for semithionine species (numbers on the curves correspond to those in table 2).

Our directly determined value based on redox titration with radicals of known redox potential is closer to the upper limit of the above estimated range.

Acknowledgements

We are grateful to Drs J P Mittal and R M Iyer for useful discussions.

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Binding of naproxen to bovine serum albumin and tryptophan-modified bovine serum albumin

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MS received 17 November 1986; revised 21 August 1987

Abstract. Two classes of binding sites, a single high-affinity site with an association constant of $4.8 \times 10^6 \text{ M}^{-1}$ and two low-affinity sites with association constant of about $0.05 \times 10^6 \text{ M}^{-1}$ have been observed in the interaction of Naproxen with bovine serum albumin (BSA). Chemical modification of two tryptophan residues in BSA with 2-hydroxy-5-nitrobenzyl bromide has led to a reduction in the association constant of the high-affinity site by 89% and its number of binding sites by 66% suggesting the involvement of tryptophan residues in the high-affinity site. In contrast, the two low-affinity sites were not affected by the modification. Binding of Naproxen to the low-affinity sites of BSA induces microdisorganisation of the albumin structure leading to conformational changes as evident from fluorescence measurements with 1-anilino-8-naphthalenesulphonic acid as the probe.

Keywords. Binding; Naproxen; bovine serum albumin; dialysis; chemical modification; fluorescence; conformational changes.

1. Introduction

Albumin is the predominant protein which binds drugs in blood and interstitial fluid (Peters 1976). The binding of a drug to proteins in the blood will strongly influence its distribution, elimination and pharmacological effect (Jusko and Gretch 1976; Martin 1965). The free concentration of a drug in plasma, on which the pharmacological activity of the drug depends, is determined by the association constant K , the number of binding sites n , and the total concentrations of the drug and the binding protein. Since the albumin molecule represents a homogeneous, well-defined and extensively studied protein with receptor-like properties (Muller *et al* 1978; Muller and Wollert 1979), bovine serum albumin (BSA) is an excellent model to study the molecular aspects of ligand-protein interaction.

The non-steroidal anti-inflammatory drug Naproxen is extensively bound to serum proteins with binding degrees above 99% (Mortensen *et al* 1979). A previous study of Naproxen-BSA interaction revealed that the binding of Naproxen to BSA is not affected by temperature and pH variations (Kaneo *et al* 1981). Besides this, detailed studies have not been made to investigate the specificity, the nature of binding sites or the amino acids involved. So it is of particular interest to

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characterize the binding of Naproxen to BSA using native BSA and chemically modified BSA (with 2-hydroxy-5-nitrobenzyl bromide) and to foresee the possible role of tryptophan residues in Naproxen binding. The fluorescent probe 1-anilino-8-naphthalene sulphonic acid (ANS) has been used in this study to get information on possible conformational changes of BSA induced by Naproxen.

2. Experimental

Bovine serum albumin (BSA) (essentially fatty acid-free) and 1-anilino-8-naphthalenesulphonic acid (ANS) were obtained from Sigma Chemical Co., USA. Naproxen was a gift from Cipla Ltd. as pure sample. 2-hydroxy-5-nitrobenzyl bromide (I-Br) was obtained from Fluka. Dialysis bags (18/32) were obtained from Wilson Laboratories, USA. All other chemicals were of analytical grade.

Binding of Naproxen to BSA was investigated by equilibrium dialysis and fluorescence techniques. All experiments were carried out at pH 7.4 in 0.05 M Na_2HPO_4 – KH_2PO_4 buffer. BSA concentration was $9.17 \mu\text{M}$. The initial Naproxen concentration, $[\text{Naproxen}]_0$ ranged from $3.0 \mu\text{M}$ to $24.0 \mu\text{M}$.

The fluorescence measurements of the solution containing ANS-BSA with or without Naproxen were determined using Aminco-Bowman Spectrophotofluorometer with excitation and emission wavelengths of 375 nm and 475 nm respectively. In these solutions, the concentration of BSA ($10.0 \mu\text{M}$) was taken in large molar excess over ANS ($0.8 \mu\text{M}$) so that ANS could bind only to its high-affinity site and its binding to its low-affinity sites is negligible. The molar ratio of Naproxen to BSA was varied from 0.2:1 to 8:1. The intrinsic fluorescence of tryptophan residues in BSA, urea-BSA and modified BSA was observed with excitation at 280 nm and emission at 350 nm.

Modification of BSA with I-Br: The two tryptophan residues in BSA were chemically modified at room temperature following the method of Karkhanis and co-workers (Karkhanis *et al* 1975; Koshland *et al* 1964) using 10 M urea and 2000-fold molar excess of I-Br. A control experiment was carried out in the same way without I-Br and this BSA is called "urea-BSA".

3. Results and discussion

Bovine serum albumin (BSA) contains two tryptophan residues and is modified selectively with 2-hydroxy-5-nitrobenzyl bromide (I-Br), as described in § 2, and is a saturable process. The degree of modification can be determined from the ultraviolet absorption quotient as described (Karkhanis *et al* 1975), from which the number of residues of I incorporated in BSA is found to be 2.5, suggesting that the modification of two tryptophan residues is selective and quantitative. Figure 1 shows that the absorbance of BSA and urea-BSA are similar, whereas that of tryptophan-modified BSA (I-BSA) is increased between 250 nm and 350 nm according to the amount of reagent incorporated and a maximum at 410 nm in the presence of free reagent. Figure 2 shows the intrinsic tryptophan fluorescence of BSA, urea-BSA and I-BSA. When compared to native BSA, the

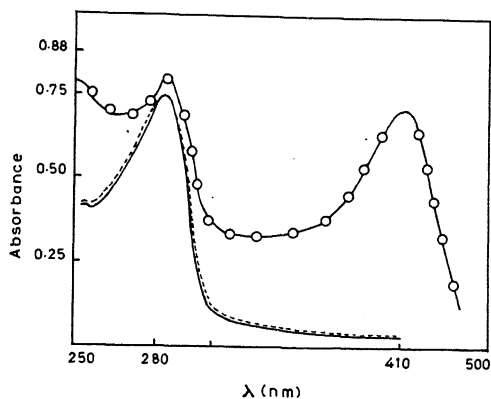


Figure 1. UV-absorption spectra of BSA (—), urea-BSA (----) and I-BSA (—○—○—○—). [BSA] = 16.0 μ M.

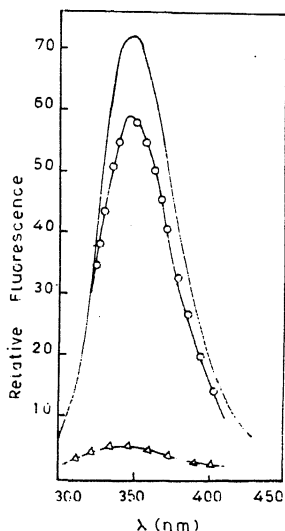


Figure 2. Fluorescence emission spectra of BSA (—), urea-BSA (—○—○—○—) and I-BSA (—△—△—△—). The spectra were recorded using an excitation wavelength of 280 nm. [BSA] = 9.17 μ M.

intrinsic fluorescence of urea-BSA is decreased by 18%, whereas it is reduced by 94% for I-BSA. The observed 18% decrease in urea-BSA is due to unfolding in acid solution, while the 94% decrease in I-BSA results from the modification of two tryptophan residues.

When the binding data of the BSA-Naproxen system, in the initial concentration range of Naproxen 3.0 μ M to 24.0 μ M, are plotted according to Scatchard (1949) in terms of r/C versus r (r = number of moles of drug bound per mole of BSA and C = [Naproxen]_{free}) a curve was obtained (figure 3) indicating more than one class of binding sites. Graphical resolution according to the method of Pennock (1973) yields two classes of binding sites, one of high-affinity and the other of low-affinity with binding constants and number of binding sites K_1 , n_1 and K_2 , n_2 , respectively. The binding parameters determined are reported in table 1.

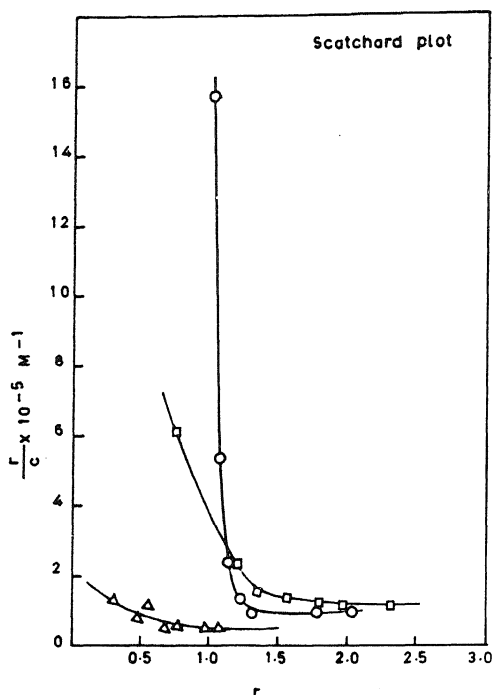


Figure 3. Scatchard plot for the binding of Naproxen to BSA ($-\circ-\circ-\circ-$), urea-BSA ($-\square-\square-\square-$) and I-BSA ($-\triangle-\triangle-\triangle-$) r = mol drug bound/mol BSA. C = equilibrium concentration of the drug. $[BSA] = 9.17 \mu M$. $[Naproxen]_0 = 3.0$ to $24.0 \mu M$.

Table 1. Binding parameters. The values are calculated from the Scatchard plot (r/C versus r) applying Pennock's method (1973) pH = 7.4; Temp. = $25^\circ C$; $[BSA] = 9.17 \mu M$ $[Naproxen]_0 = 3.0 \mu M$ to $24.0 \mu M$.

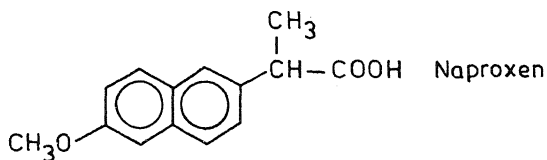
	$K_1 \times 10^{-6}$ (M^{-1})	n_1	$K_2 \times 10^{-6}$ (M^{-1})	n_2
BSA	4.800	1.00	0.050	2.00
Urea-BSA	3.420	0.76	0.051	2.24
I-BSA	0.529	0.34	0.037	1.60

From table 1 it can be seen that Naproxen has one high-affinity site with $K_1 = 4.8 \times 10^6 M^{-1}$ and two low-affinity sites with $K_2 = 0.05 \times 10^6 M^{-1}$ in native BSA. Naproxen is one of the drugs strongly bound by serum proteins (Mortensen *et al* 1979). Strongly bound drugs have been shown to possess "receptor-like" specificity (McMenamy and Oncley 1958; Muller and Wollert 1973) and it is reported that this specific nature is mediated by only a small number of binding sites (Sudlow *et al* 1975, 1976). Hence, the high K_1 value observed represents the strong single binding site in BSA. When K_1 and K_2 values are compared, it is found that the K_1 value is 96 times greater than the K_2 value. This difference in K values is manifested not only due to the vast difference in the affinity of the two classes of

sites, but also due to the dissimilar specificity and structural requirements. From the association constant values it can be deduced that the high-affinity site is highly specific and its structural characteristics are different from the two low-affinity sites.

When Naproxen binds to urea-BSA, K_1 and n_1 values decrease to $3.42 \times 10^6 \text{ M}^{-1}$ and 0.76, respectively (table 1). The reduction seems to be of low significance as there would have been a larger decrease if the specificity of the high-affinity sites were lost. The decrease is attributed to acidic unfolding in urea solution at pH 4.4 and an incomplete refolding when the pH is raised to 7.4. The values of K_2 and n_2 are found to be unaltered.

When Naproxen binds to I-BSA, in which the two tryptophan residues are chemically modified, K_1 and n_1 values are reduced to $0.529 \times 10^6 \text{ M}^{-1}$ and 0.34, respectively. The observed decrease of 89% and 66% in K_1 and n_1 values, respectively, occurs due to the loss of the affinity of the site. Naproxen is an arylpropionic acid drug.



The presence of a hydrophobic area in BSA is essential in order to have a strong hydrophobic interaction with Naproxen. Further, the inevitable presence of the one tryptophan residue in this hydrophobic area (since tryptophan is the most nonpolar of all amino acids) is necessary to provide the needed specificity, hydrophobicity and structural requirements. The specific and quantitative modification of these residues results in the loss of specificity and structural characteristics leading to the observed reduction in K_1 and n_1 values. Hence the presence of tryptophan fulfils the structural features required for the binding of Naproxen to its high-affinity site.

The K_2 and n_2 values for the binding in I-BSA are reduced by 26% and 20%, respectively, which precludes the possibility of the involvement of the tryptophan residues in the low-affinity sites. The difference in the characteristics and the specificity of the two classes of sites is confirmed as the structural requirements of the two low-affinity sites do not require the presence of the tryptophan residues to be part of the sites.

Conformational changes induced by Naproxen: Changes in the conformation of albumin as a result of binding of small molecules has been observed previously (Blanchar *et al* 1975; Krieglstein 1969; Scholtan 1964; Uchida and Hanano 1974), and these changes were detected by monitoring the fluorescence of bound probes. Fluorescent probe techniques monitor only small areas of protein molecule and hence conformational changes observed may be relatively localised. In order to monitor the conformational changes, the limiting condition at which the probe is completely bound to BSA is used. The probe used in this study is 1-anilino-8-naphthalene sulphonic acid, which binds preferably to the hydrophobic site of the BSA. ANS-BSA emits at 475 nm when excited at 375 nm. When the ratio

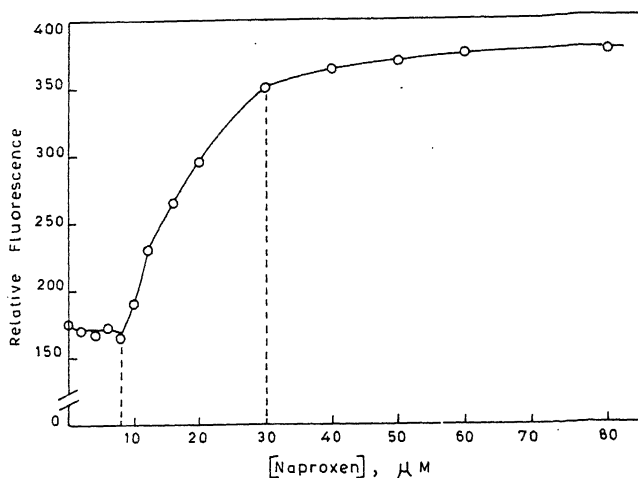


Figure 4. Effect of increasing concentration of Naproxen on the fluorescence of ANS-BSA complex. $[\text{ANS}] = 0.8 \mu\text{M}$; $[\text{BSA}] = 10.0 \mu\text{M}$. Excitation and emission wavelengths are 375 nm and 475 nm respectively.

$[\text{ANS}]/[\text{BSA}]$ is 0.08, where the limiting condition is obeyed, it represents a condition, sensitive to the changes in protein structure around the binding sites of the probe as observed elsewhere (Birkett *et al* 1977).

Increasing amounts of Naproxen were added to ANS-BSA mixture at the limiting condition, such that drug to BSA ratio varied from 0.2:1 to 8:1. The fluorescent emission was unaltered by addition upto the drug: BSA ratio of 0.8:1 (figure 4), at which value Naproxen would bind to its high-affinity site only. The microenvironment which is sensitive under this limiting condition is unaltered leading to this negligible change. Further addition of Naproxen upto a drug: BSA ratio of 3:1, when the drug also binds to its low-affinity sites causes increase in fluorescence by 200% (figure 4), above which further addition causes negligible increase. The occupation of the two low-affinity sites by Naproxen causes conformational changes in protein (BSA) structure around ANS-BSA binding site resulting in the microdisorganisation of the ANS-BSA microenvironment leading to predominant increase in fluorescence.

Thus the binding of Naproxen to its high-affinity site does not cause conformational changes, whereas binding to its low-affinity sites leads to disorganisation of the microenvironment resulting in localised conformational changes. The above mentioned difference between the two classes of sites confirms the tryptophan modification studies, where distinction arises out of dissimilar structural specificities of the sites, the high-affinity site requiring tryptophan residues to be part of its site whereas the two low-affinity sites do not require tryptophan residues for the binding.

Acknowledgement

This work was supported by CSIR New Delhi. The authors wish to thank Cipla Ltd., India for providing a pure sample of Naproxen.

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On the $\pi^2S + \pi^2S$ pathways toward $[n]$ -prismanes

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MS received 25 September 1987

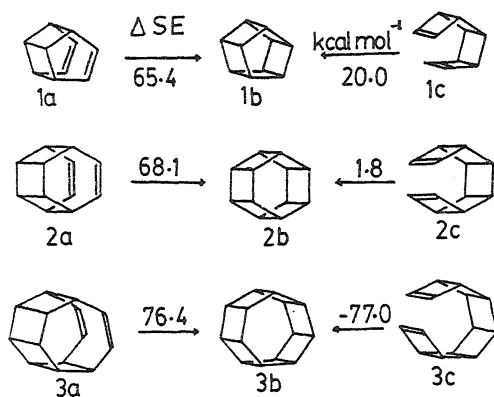
Abstract. Empirical force field calculations indicate that 1c, 2c and 3c rather than 1a, 2a and 3a are more favourable precursors for photocycloadditions to give $[5]$ -, $[6]$ - and $[7]$ -prismane respectively.

Keywords. $[n]$ -Prismanes; photocycloaddition; strain energy.

There is considerable experimental and theoretical interest in the higher members of the $[n]$ -prismanes (Reddy and Jemmis 1986; Eaton *et al* 1981; Mehta and Padma 1987; Yang and Horner 1986; Mehta *et al* 1987; Allinger and Eaton 1983). The last step in many of the planned synthesis is a photochemical $\pi^2S + \pi^2S$ cycloaddition (scheme 1. 1a $\rightarrow$ 1b, 2a $\rightarrow$ 2b, 3a $\rightarrow$ 3b). Unfortunately these are not successful (Mehta and Padma 1987; Eaton *et al* 1986; Mehta *et al* 1987). In this communication we analyse the problems with these reactions and suggest alternative precursors which have never been considered before.

There are several factors working against these reactions. The major hurdle is the construction of three cyclobutane rings in one step. If an average of 20 kcal/mol of strain is assumed for each cyclobutane the strain energy increase would be 60 kcal/mole on this count alone. Besides there are considerable destabilizing changes in the CCC angles in the products of these reactions. 2a, for example, has comfortable angles around the sp^2 carbon but the angles cannot change much during the formation of 2b though the carbons become tetra-coordinate. These are reflected in the large strain energy differences (ΔSE) calculated for them using empirical force field calculations (Allinger 1977, Allinger and Yuh 1980).

The two unfavourable factors can be avoided by a small change in the precursors. Consider 1c, 2c and 3c where the double bonds are parallel to the C_n axis of the target prismanes. Only one four-membered ring will be added as a consequence of the 2+2 addition now. The change of angle at the trigonal carbons is not very large, but the carbon centre has become 'tetrahedral' so that the initial small angle is better accommodated. In addition to these the two ethylene units in 1c, 2c and 3c should be close together. The all-cis-fused four-membered rings bring them close.



Empirical force field calculations (scheme 1) show that ΔSE s for cycloaddition of 1a, 2a and 3a are larger than 50 kcal/mol, an empirical limit arrived at previously beyond which the reactions may not take place (Osawa *et al* 1977; Mehta *et al* 1987). According to the same criterion 1c, 2c and 3c should react easily. There is only an increase of 20 kcal/mol of strain in going from 1c to 1b, well within the limits of ΔSE mentioned above. The ethylenes are close to each other (adjacent C-C distances are 2.9 Å each). The reaction 2c $\rightarrow$ 2b should be a facile one. With 3c, the prismane becomes the less strained species. Should it be possible to make 3c, conversion to 3b should not pose any problems. Though the precursors 1c, 2c and 3c may be more difficult to prepare because of the all cis-fused rings, attempts in this direction should be rewarding.

Acknowledgements

We thank the UGC, New Delhi (COSIST Programme to School of Chemistry), for the purchase of a microcomputer used in this study.

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Schiff bases of nickel(II), copper(II) porphyrins and dibenzo-18-crown-6 interspersed *bis*-metal porphyrins. Protonation studies

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MS received 3 September 1987; revised 4 December 1987

Abstract. Schiff-base (SB) derivatives of Ni(II) and Cu(II) porphyrins endowed with various amine functions (R-NH₂), *n*-butylamine, *p*-anisidine and *m*-nitroaniline have been prepared from corresponding formyl porphyrins. Protonation studies of these SB derivatives reveal a marked red shift of the optical absorption bands in the visible region relative to the unprotonated imines. The magnitude of the observed red shifts in the protonated derivatives, (SBH⁺) are found to depend on the electron-withdrawing or electron-donating nature of the R group of the amines. The results of the optical absorption, ¹H NMR, EPR, and cyclic voltammetric studies are illustrative of the fact that protonation of the SB derivatives results in a localized positive charge, P-C(H) = N⁺(H)-R in the periphery of the porphyrin (p) system. The dibenzo-18-crown-6 interspersed *bis*porphyrin schiff bases have been prepared from *trans* 4,4'-diamino dibenzo-18-crown-6 and formyl porphyrins. The protonation of these SB derivatives is found to proceed in a concerted fashion. The cation complexation studies by the crown ether entity in the *bis*porphyrin systems have been investigated using optical absorption, magnetic resonance and electrochemical methods. The redox characteristics of the protonated dimeric SB porphyrins reveal that the first oxidation step involves a two-electron transfer reaction. This is important in view of their possible usage in multielectron transfer reactions of biological and catalytic interest.

Keywords. Schiff-bases of porphyrins; metal porphyrins; protonation studies; crown ether.

1. Introduction

In recent years considerable attention has been focussed on the protonation behaviour of Schiff-base porphyrins. Interest in these investigations lies in the observation of large red-shifts of the long wavelength absorption bands of the Schiff base porphyrins on protonation. These findings closely parallel the red shifts observed in the visible bands of *in vivo* chlorins and bacteriochlorins in plant and bacterial photosystems (Katz *et al* 1978; Sauer 1979). The red-shift of the long wavelength band of the protonated Schiff base (SBH⁺) relative to the unprotonated imine (SB) has been explained in terms of localized positive charge in the vicinity of tetrapyrrole moiety (Ward *et al* 1984; Hanson *et al* 1984; Maggiora *et al* 1985). In all the model studies, the SB formation involves the condensation of the formyl/keto group (situated at the porphyrin periphery) with butyl amine. In view of the fact that the transition energies of the visible band of the SBH⁺ species are

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affected by the extent of localization of the positive charge, it would be of interest to study the influence of the nature of the amines (electron-withdrawing and electron-donating) and metal ions on the optical absorption feature of the SBH^+ species. Moreover, the covalently linked *bis*porphyrins bearing Schiff-base linkages offer interesting models to probe into the changes in optical absorption features that can occur from cooperative interactions of the two constituent monomeric Schiff base units. In addition, these *bis*porphyrins provide an opportunity to study the mutual metal-metal interactions and the influence of a positive charge (in the periphery of SBH^+) on such interactions.

Here we report the synthesis and spectral properties of both monomeric and dimeric Ni(II) and Cu(II) Schiff base porphyrins and their protonated derivatives. The choice of Cu(II) and Ni(II) porphyrins are necessitated by their inertness towards demetallation. The SB porphyrins bear both aliphatic (butyl amine) and aromatic (*p*-anisidine and *m*-nitroaniline) amines to study the effect of electron-donating and electron-withdrawing groups on the protonation behaviour and the optical properties of the resulting SBH^+ species. Novel dimeric Ni(II) and Cu(II) porphyrin Schiff-bases wherein a crown ether, dibenzo-18-crown-6, moiety forms the Schiff base covalent bridge between the two porphyrin units have been prepared. In addition to investigating the possibility of step-wise protonation in these *bis*porphyrins, we explored the utility of crown-ether interspersed *bis*porphyrins as ionophores. The optical absorption, ^1H NMR and EPR spectral data of these SB and SBH^+ species provide valuable information concerning the mode of protonation of these SB porphyrins and their electronic structures.

2. Experimental

2.1 Materials

Nickel(II) and copper(II) meso-tetraphenyl porphyrin aldehydes MTPP-CHO were synthesised making use of the procedure of Momenteau *et al* (1979). The *trans* 4,4'-diamino-dibenzo-18-crown-6 was prepared according to the earlier described procedure (Thanabal and Krishnan 1981). The amines, *n*-butyl amine, *p*-anisidine and *m*-nitroaniline were procured from Aldrich Chemicals (USA) and used as received. All the solvents employed in the study were distilled and dried before use. Representative preparation of Schiff-base porphyrins are given below.

2.1a Schiff base of NiTPP and *p*-anisidine: A solution containing 0.10 g of NiTPP-CHO in 100 ml toluene and 0.20 g of *p*-anisidine dissolved in minimum amount of CH_3OH was refluxed for 4 h. At the end of this period, the solvent was removed under reduced pressure and the residue was quickly washed with CH_3OH to remove the excess amine. The product was crystallized from $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (1:1 by vol) solvent mixture.

2.1b Schiff base of NiTPP/CuTPP and diaminodibenzo-18-crown-6: To a 0.50 g of CuTPP/NiTPP-(CHO) in 200 ml of toluene, 0.015 g of *trans* 4,4'-diamino-dibenzo-18-crown-6 in 10 ml of CH_3OH was added slowly over a period of 30 min. This solution was refluxed for 3 h and the solvent was removed under reduced

pressure. The residue was washed with CH_3OH several times to remove the unreacted amine. The product was taken in CHCl_3 and chromatographed on a neutral alumina column. The dimer was obtained after elution with CHCl_3 .

The Schiff base complexes prepared in this study are shown in figure 1. The yields in all the cases were about 10% based on the porphyrin-aldehyde. It is found that repeated chromatography degrades the Schiff bases.

2.2 Methods

Schiff base protonation/deprotonation were performed according to the following procedure. Air, equilibrated over concentrated HCl was bubbled through a 100 ml solution of SB in CHCl_3 . The progress in protonation was monitored by following the increase in absorbance at 620 nm. The protonation of SB is also accomplished by successive addition of CF_3COOH . The deprotonation reaction was carried out either by bubbling air saturated with triethyl amine or by the addition of pyridine in

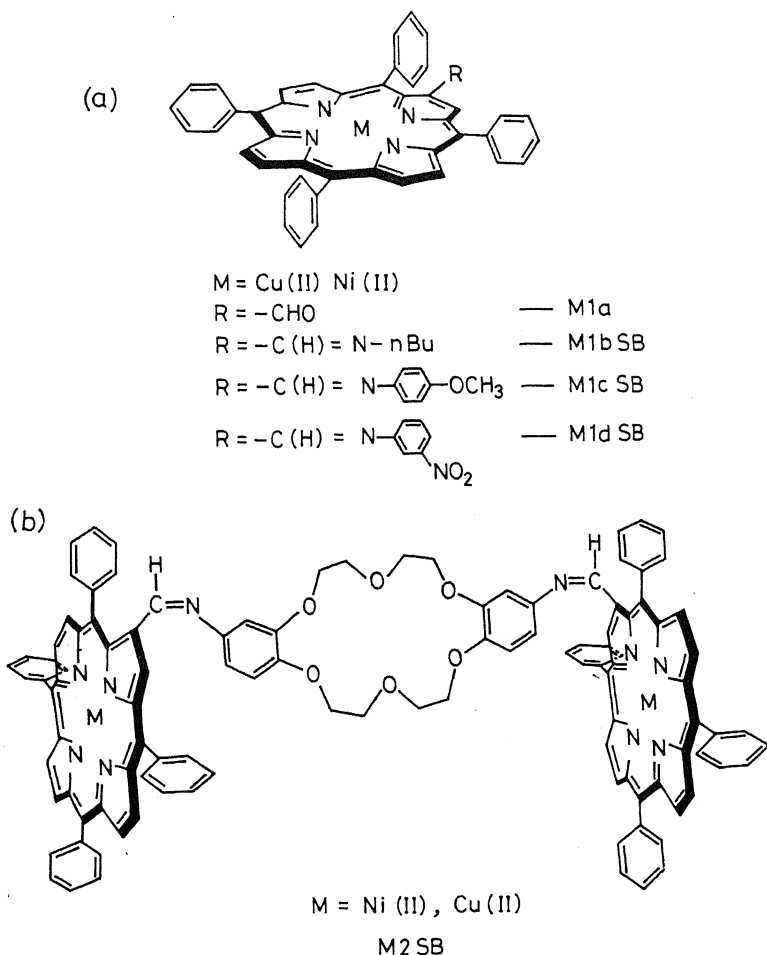


Figure 1. The chemical structures of (a) monomeric, and (b) dimeric Schiff-base complexes of Ni(II) and Cu(II) porphyrins.

dry ether to the acidified solution of SB. Sufficient care was taken to avoid the entrance of moisture when carrying out all the above reactions.

It is important to note that the features observed during the protonation/deprotonation of dimeric SB porphyrins are essentially the same as that observed for monomeric SB porphyrins. We have not been able to identify any monoprotinated form of the dimeric SB porphyrin. Spectroscopic and electrochemical measurements were carried out on instruments described earlier (Bhaskar Maiya and Krishnan 1985).

3. Results and discussion

The SB derivatives of the metalloporphyrins have been synthesised from the corresponding formyl compounds. The structural integrity of these compounds has been established from the absorption spectral and ^1H NMR data.

The absorption spectral profiles of CuTPP, CuTPP(CHO), and Cu1bSB in CHCl_3 are shown in figure 2. It is observed that the Q bands of the porphyrins are red-shifted on formylation. The porphyrin Schiff bases exhibit absorption bands at shorter wavelengths relative to the formylated products. Dramatic changes in the absorption spectral features of SB porphyrins are observed on protonation of these compounds with $\text{CF}_3\text{COOH}/\text{HCl}$. Successive addition of the acid to the SB derivatives of Cu(II) and Ni(II) porphyrins results in very large spectral shifts of the Q bands to the red region and a splitting/broadening of B bands (figure 3). The absorption data of all SB porphyrins and their protonated analogues are given in table 1. It can be seen that SBH^+ species [Ni(II) and Cu(II) derivatives of Ic and Id, and dimeric SB] endowed with aromatic side groups exhibit a larger red shift (40 nm) of the Q bands relative to the SBH^+ compounds bearing aliphatic side groups [Ni(II)/Cu(II)1bSB]. It is found that the magnitudes of these red shifts are independent of the nature of the metal ion. This suggests that the changes in the absorption profiles are due to the localized charges on the periphery of the porphyrins and absence of any M-N (σ or π bond) interaction with the peripheral charge. Significantly, addition of bases, pyridine or triethylamine, to the SBH^+ species returns the original spectrum of SB indicating that the protonation is a completely reversible process. It is of interest to note that the magnitude of the spectral shifts and the shapes of the red-shifted bands observed on protonation of the *bis*porphyrin Schiff-bases are not different from the corresponding monomeric protonated Schiff bases. This implies that the protonation occurs in a concerted fashion and the spectral changes are a consequence of the electronic structure of the SBH^+ species. The origin of the spectral shifts in SBH^+ could be either due to the delocalization of the positive charge on the ring or to the localization of the hole on the periphery in an electron-deficient group in conjugation with the ring. In order to investigate the effect of the latter, we synthesized an ethylcyanoacetate adduct of CuTPP(CHO)/NiTPP(CHO) in which the substituent at the periphery of the porphyrin is electron-withdrawing but coulombically neutral. The absorption spectral features of these adducts closely resemble the features observed for SBH^+ derivatives (table 1). This suggests that the charge in SBH^+ is localized on the macrocycle. The presence of a positive charge in the porphyrin periphery can lead to the lowering of the energy of the π^* orbital of $-\text{C}(\text{H}) = \text{N}^+(\text{H})-\text{R}$ entity of SBH^+

causing a perturbation of π^* (e_g) orbitals of the porphyrin macrocycle resulting in the red-shift of the Q bands of SBH^+ . These effects are investigated using magnetic resonance spectroscopy.

The proton NMR spectra of $\text{NiTPP}(\text{CHO})$, NiIcSB and the corresponding SBH^+ in CDCl_3 are shown in figure 4. It is found that all the proton resonances, β -pyrrole (8.90–8.60 ppm), o -mesoaryl (8.00–7.80 ppm) and m and p meso aryl (7.78–7.60 ppm) groups of the porphyrin aldehyde are shifted marginally in the corresponding Schiff bases. Of particular interest is the shift in the proton resonance of $\text{NiTPP}(\text{CHO})$ at 9.20 ppm to 9.30 ppm on imine, $-\text{C}(\text{H}) = \text{N}-\text{R}$, formation. The resonances originating from the R group are assigned based on comparison with the resonance spectrum of $\text{NiTPP}(\text{CHO})$. We observed dramatic changes in the proton resonances of SB on protonation. It is found that the

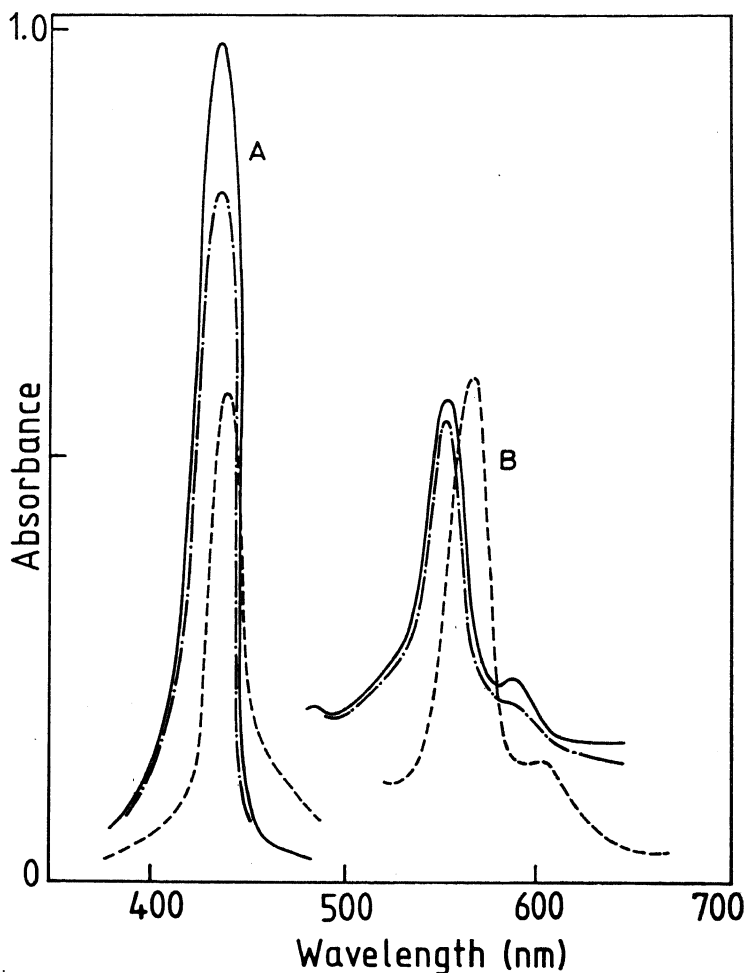


Figure 2. Optical absorption spectral profiles of CuTPP (—), CuTPPCHO (---) and CuIcSB (-·-·-) in CHCl_3 at 298 K. (A) The concentrations employed are 1.0 to 4.0 μM . (B) The concentrations employed are 0.1 to 0.4 mM.

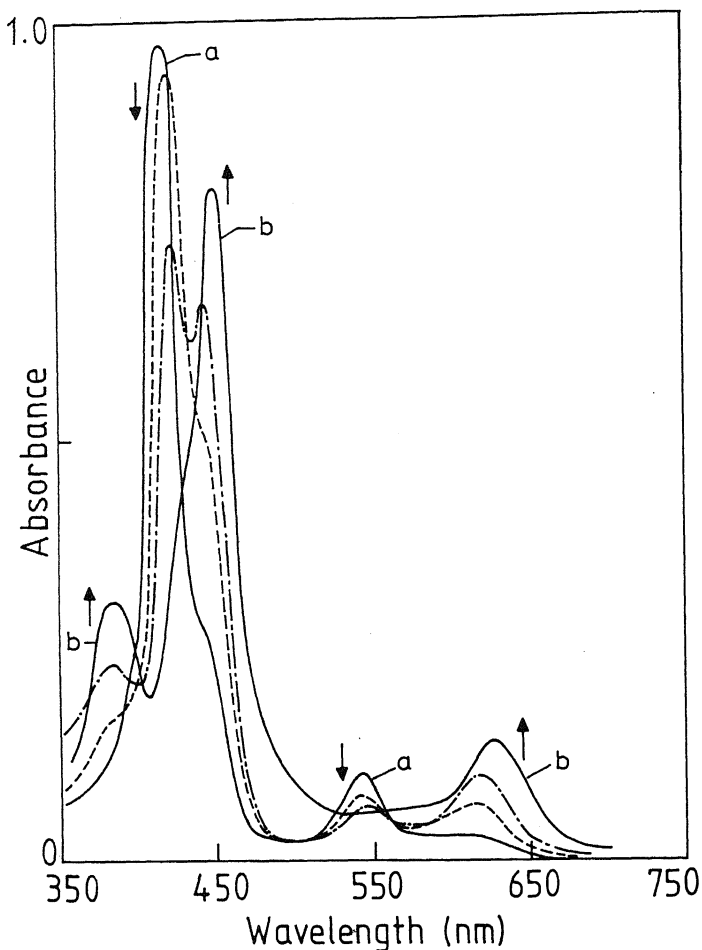


Figure 3. Optical absorption spectral changes observed on successive addition of CF_3COOH to CuIbSB in CHCl_3 at 298 K. (a) CuIbSB and (b) completely protonated derivative CuIb2SH^+ . The concentration of CuIbSB employed is 1.0–2.0 μM .

resonances of the protons close to the positive charge, $-\text{C}(\text{H}) = \overset{+}{\text{N}}(\text{H})\text{R}$, are progressively shifted to higher fields and broadened. On the other hand, the β -pyrrole and *meso* aryl proton resonances occur around the same field as that observed for the SB indicating that these protons are less affected by protonation. Interestingly, the proton bonded to the carbon in $-\text{C}(\text{H}) = \overset{+}{\text{N}}(\text{H})\text{R}$ resonates in the upfield region relative to its position at 9.30 ppm in the SB. We ascribe this to the shielding effect induced on protonation and to the π -electron anisotropy experienced by the $-\text{C}(\text{H}) = \overset{+}{\text{N}}(\text{H})\text{R}$ group. It is noteworthy that the presence of a positive charge on the nitrogen of the SBH^+ results in the deshielding and broadening of the proton resonances of the R group. The latter decreases with increasing distance between the positive charge and the R group. These findings

Table 1. Visible spectral data on Schiff-base complexes and their protonated species in CHCl_3 at 298 K^a.

Compound	λ (nm)			
	Q_1	Q_2	B_2	B_1
CuTPP	580	541	417	
CuIa	590	551	429	
CuIbSB	580	545	419	
CuIbSBH ⁺	628		452	387
CuIcSB	587	549	425	
CuIcSBH ⁺	643		476	397
CuIdSB	587	547	431	
CuIdSBH ⁺	648		476	396
Cu2SB6	587	549	425	
Cu2SBH ⁺ ^b	646		474	394
NiTPP	573		416	
NiIa	576	538	428	
NiIbSB	575	536	422	
NiIbSBH ⁺	615		446	380
NiIcSB	580	540	426	
NiIcSBH ⁺	638		472	390
NiIdSB	583	541	429	
NiIdSBH ⁺	640		475	395
Ni2SBb	580	537	427	
Ni2SBH ⁺ ^b	650		475	380
Ni-ethyl cyano acetate adduct	667		448	

^a Protonation was achieved by adding HCl or CF_3COOH ;^b Addition of Cs^+ to these dimeric porphyrins does not alter the spectral features.

collectively show that the protonation of the SB is similar to the effect of creating an exceptionally strong electron-withdrawing group in the periphery of the macrocycle.

It would be of interest to study whether there exists any electronic coupling of the π -system and the peripheral positive charge. The Schiff bases of Cu(II) porphyrins are chosen to study these effects using EPR spectroscopy. The EPR spectra of CuIdSB and the corresponding SBH^+ in toluene at 100 K are shown in figure 5. The spectra were analysed using the spin Hamiltonian for axial symmetry (Assour 1965). The values of g and A tensors have been calculated for all the monomeric and dimeric SB derivatives, and their corresponding protonated species (table 2). It is found that the EPR spectral features of SB and SBH^+ species are similar and the magnitudes of the g and A values do not markedly change in SB and in the protonated SBH^+ complexes. These two observations indicate that the hole created at the porphyrin periphery is not electronically coupled with the π -system so as to create a perturbation at the Cu(II) centre. This also suggests the absence of any Cu(II)-Cu(II) interaction in the crown ether interspersed dimeric Schiff base derivatives of Cu(II) porphyrins (Thanabal and Krishnan 1982). The possibility of axial coordination of the added proton donors $\text{CF}_3\text{COOH}/\text{HCl}$ to the Cu(II) centre is discarded since the g and A values do not increase in the SBH^+ species relative to

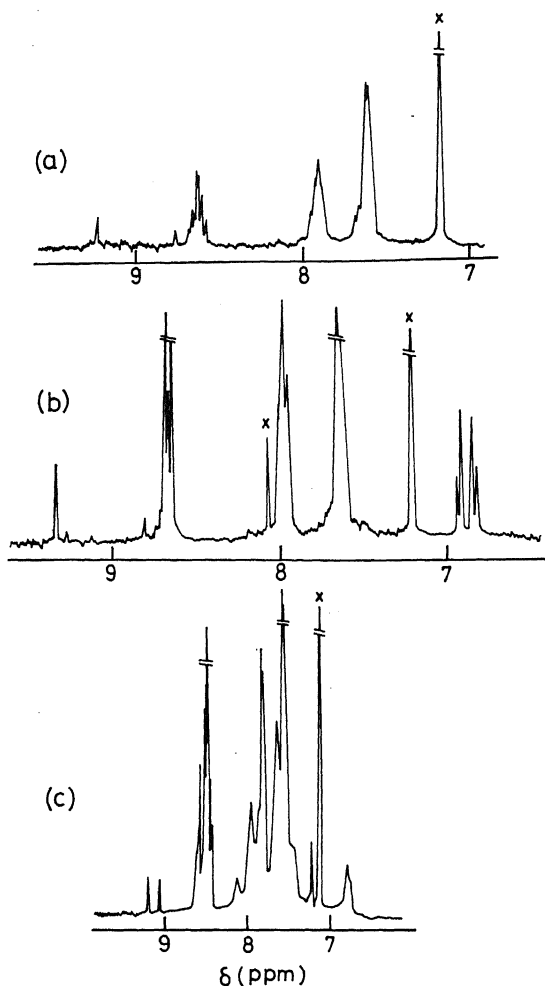


Figure 4. The ^1H NMR spectra of (a) NiTPPCHO, (b) NiIcSB and (c) NiIcSBH $^+$, in CDCl_3 at 298 K. NiIcSBH $^+$ is produced on addition of CF_3COOH to NiIcSB. Solvent impurity peaks are marked X.

those observed for the corresponding SB (Chandrashekar and Krishnan 1981, 1982). The marginal changes in EPR parameters in SBH $^+$ relative to SB can be ascribed to the inductive effects of the peripheral electron-withdrawing group, $-\text{C}(\text{H}) = \dot{\text{N}}(\text{H})-\text{R}$.

It is known that the redox properties of the porphyrins are strongly influenced by the electron-donating or -withdrawing nature of the substituents (Felton 1978). The cyclic voltammograms (CV) of the various SB and their protonated complexes have been studied to elucidate the effect of the substituents on the redox potentials. The CV of CuIbSB and its derivatives in the anodic region are shown in figure 6. The two reversible peaks observed in the region 0–1.50 V correspond to the successive one-electron transfers from the porphyrin ring. This is confirmed by the analysis of

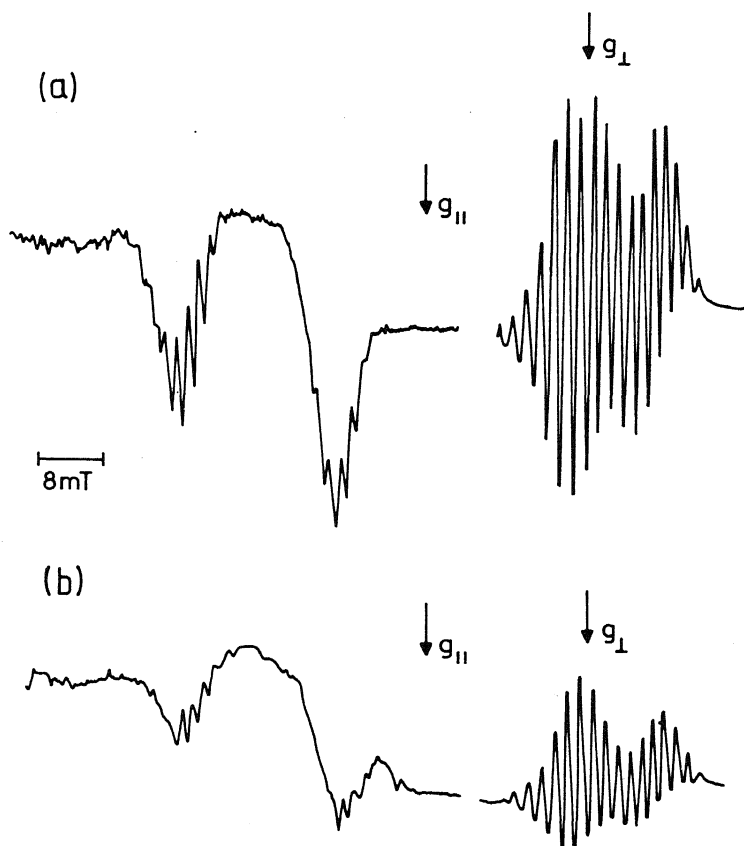


Figure 5. EPR spectra of (a) CuIdSB, and (b) CuIdSBH⁺ in toluene at 100 K. CuIdSBH⁺ is produced by addition of HCl to CuIdSB.

Table 2. EPR data on Cu(II) derivatives of Schiff-base complexes and their protonated analogues in toluene at 100 K.

	g_{11}	$g_{\perp}$	A_{11}^{Cu}	$A_{\perp}^{\text{Cu}}$	A_{11}^{N}	$A_{\perp}^{\text{N}}$
				$(\times 10^{-4} \text{ cm}^{-1})$		
CuTPP	2.185	2.047	208.0	31.5	14.8	16.0
CuIa	2.152	2.013	196.0	31.0	14.3	15.5
CuIbSB	2.167	2.029	198.0	31.9	14.3	16.0
CuIbSBH ⁺	2.173	2.023	198.0	31.1	14.4	15.7
CuIcSB	2.157	2.022	201.0	31.3	14.3	15.5
CuIcSBH ⁺	2.160	2.020	205.0	30.0	14.6	15.4
CuIdSB	2.158	2.020	200.0	31.2	14.3	15.6
CuIdSBH ⁺	2.159	2.024	201.0	31.2	14.4	15.5
Cu2SB	2.138	1.989	207.0	31.1	15.0	15.6
Cu2SBH ⁺ ^a	2.160	2.019	*	31.4	*	15.7
Cu2SBH ⁺ + Cs ⁺ ^a	2.138	1.985	207.0	30.8	15.1	15.7

^a Spectra were taken in CH₃OH:CH₂Cl₂ (1:1, V/V) solvent mixture; * Spectrum is not well resolved to calculate these values.

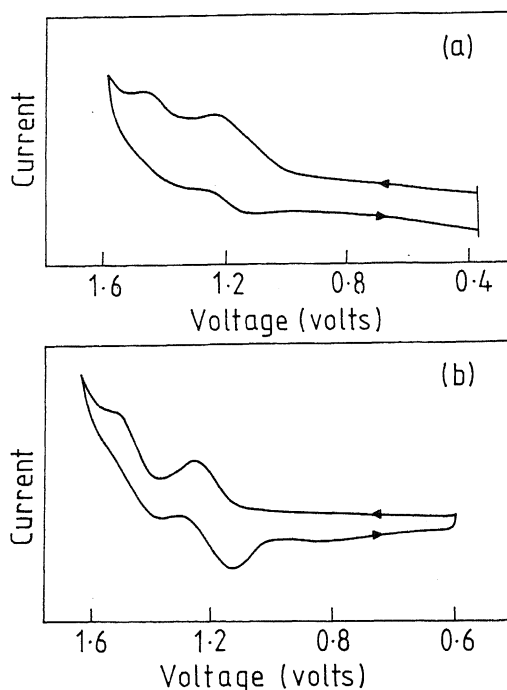


Figure 6. Cyclic voltammograms of (a) CulbSB, and (b) CulbSBH⁺, in CH₂Cl₃ containing 100 mM TBAP at 298 K. Scan rate 50 mV/s. CulbSBH⁺ was produced on addition of CF₃COOH to CulbSB. Potentials are with respect to SCE.

current-voltage profiles at different scan rates. The electrochemical data obtained for all other Cu(II) and Ni(II) derivatives are given in table 3. An inspection of the table reveals that the SB porphyrins exhibit ring oxidation potentials in a lower anodic region relative to that of the porphyrin-aldehyde, while on protonation, the SBH⁺ species exhibit ring oxidation at a higher anodic potential relative to the SB. This shows that the addition of acid renders the electron removal from the porphyrin more difficult suggesting that the $-\text{C}(\text{H})=\text{N}^+(\text{H})-\text{R}$ group situated at the periphery of the porphyrin is indeed a strong withdrawing group.

The electrochemical redox data has provided information on the relative energy difference between the HOMO and the LUMO in the various synthesized porphyrin aldehydes, Schiff bases and their corresponding protonated species. The difference between the first oxidation potential and the reduction potential of the porphyrin ring can be approximated to the energy difference between the HOMO and the LUMO in the porphyrins (Fuhrhop 1974). It is observed that the energy difference between the HOMO and the LUMO in the SB porphyrins are marginally higher than the porphyrin aldehydes. This affords an explanation of the blue shift of the *Q* bands observed on SB formation. It was earlier suggested that in the SBH⁺ species, there is considerable mixing of the π^* orbital of the substituent with the e_g (π^*) orbital of the porphyrin ring leading to the stabilization of the latter orbital. This suggests that the reduction of the substituent group should occur at a higher cathodic potential relative to the free state. Though we are unable to probe into the reduction of the substituent electrochemistry, the trend in the oxidation

Table 3. Redox potentials of Schiff-base and their protonated complexes in CH_2Cl_2 at 298 K^a.

Compound ^b	$P \longrightarrow P^{+\cdot}, V$	$P^{+\cdot} \longrightarrow P^{2+}, V$	$P \longrightarrow P^{\cdot-}, V$
CuTPP	1.01	1.26	-1.29
CuIa	1.08	1.32	-1.11
CuIbSB	1.15	1.38	-1.26
CuIbSBH ⁺	1.18	1.36	
CuIcSB	1.14	1.45	-1.21
CuIcSBH ⁺	1.16	1.49	
CuIdSB	1.16	1.37	-1.16
CuIdSBH ⁺	1.26	1.43	
Cu2SB	1.01	1.35	-1.19
Cu2SBH ⁺	0.94 ^c		
NiTPP	1.18		-1.21
NiIa	1.15		-1.10
NiIbSB	1.19		-1.22
NiIbSBH ⁺	1.23		-1.26
NiIcSB	1.25		-1.22
NiIcSBH ⁺	1.26		
NiIdSB	1.25		-1.20
NiIdSBH ⁺	1.21		
Ni2SB	1.19		-1.16
Ni2SBH ⁺	1.12 ^c		

^a Potentials are reported with respect to SCE. Error: ± 20 mV.^b P, P^{+\cdot}, P²⁺ and P^{\cdot-} refer to neutral, monocation radical, dication and monoanion radical species of the corresponding porphyrins, respectively.^c Represents two-electron transfer.

potentials of the SBH⁺ species indicate that the energy differences between the HOMO and the LUMO are lower than in the corresponding SB porphyrins. This provides an explanation of the red shift of the *Q* bands observed for SBH⁺ species.

Of special interest is the electrochemical behaviour of dimeric SBH⁺ derivatives of Cu(II) porphyrins. Earlier studies on *bis* Cu(II) systems reveal that the Cu(II)-Cu(II) interactions are easily manifested in the magnitudes of the oxidation/reduction potentials (Collman *et al* 1979; Liu *et al* 1983). The CV of the *bis* Cu(II) derivative, Cu2bSB, in CH_2Cl_2 exhibits a reversible peak (figure 7) at 1.01 V involving one-electron oxidation of the porphyrin ring. This shows that the porphyrin rings are essentially non-interacting in the *bis* Cu(II) derivatives (Collman *et al* 1980; Leznoff *et al* 1984). Interestingly, on protonation, the SBH²⁺ species exhibit a potential at 0.94 V involving a two-electron oxidation in contrast to the one-electron oxidation of the corresponding non-protonated Schiff base (figure 7). This seems to suggest that the presence of a positive charge on the periphery of the porphyrins in the *bis* Cu(II) derivatives possibly alters the mechanism of heterogenous electron transfer (Nicholson 1965). We believe that the two porphyrin rings in the dimer respond to oxidation independently and that the interaction between them is weak since the two rings are separated by more than 10 Å and the covalent bridge that exists between them is conformationally rigid.

In our earlier studies, we demonstrated the utility of cavity-bearing porphyrins as efficient ionophores (Dasgupta *et al* 1982). We investigated the ionophore

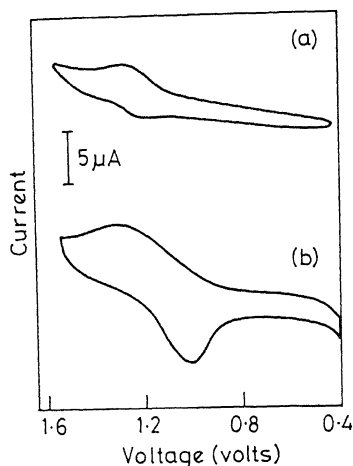


Figure 7. Cyclic voltammograms of (a) Cu2bSB, and (b) Cu2bSBH₂²⁺, in CH₂Cl₂ containing 100 mM TBAP at 298 K. Scan rate 50 mV/s. SBH₂²⁺ was produced on addition of CF₃COOH to SB. Potentials are with reference to SCE.

behaviour of *bis*Cu(II)/Ni(II) porphyrins bearing a dibenzo-18-crown-6 cavity. Of special importance is the study of the complexation behaviour of *bis*porphyrins with those cations which require two dibenzo-18-crown-6 cavities, since the cation encapsulation can result in the dimeric derivatives of the *bis* Cu(II)/Ni(II) porphyrins similar to the cation-induced dimers of crown ether porphyrins (Thanabal and Krishnan 1982). It is known that the Cs⁺ ion forms 1:2 (cation : dibenzo-18-crown-6) complexes with crown ether (Pedersen 1967). It is observed that the addition of CsCl/CsCNS solution (CH₃OH : CHCl₃ 1:1 by vol) to the Cu2SB/Ni2SB or their protonated derivatives in the same solvent mixture does not produce any shifts in *Q* or *B* absorption bands of the porphyrins. However, the ¹H NMR spectra of a solution containing Ni2SB/Ni2SBH₂²⁺ in CD₃OD/CD₃CN and Cs⁺ ion reveal broadening of the proton resonances of the ether fragments in the region 3.00–4.00 ppm suggesting Cs⁺ complexation with the crown ether (Live and Chan 1976). Owing to poor resolution of the ¹H NMR spectrum, it is difficult to assess the extent of complexation in these systems. We investigated the EPR spectra of Cs⁺ complexes of Cu2SBH/Cu2SBH₂²⁺ in toluene at 100 K in the anticipation of detecting axial dimers of *bis* Cu(II) SB and its promoted derivatives. The EPR parameters of the Cs⁺ complexes reveal no significant change in *g* and *A* tensor values and show the absence of $\Delta m = \pm 2$ transitions. This indicates that the complexation of Cs⁺ ion does not result in dimers of *bis* Cu(II) SB derivatives possessing axial symmetry. The presence of Cs⁺ ion in the dibenzo-18-crown-6 cavity of the *bis* Cu(II)/Ni(II) SB porphyrins and their protonated species does not alter the ring oxidation/reduction potentials of these porphyrins. It is of interest to note that the oxidation potentials of Cs⁺ complexes of protonated derivatives involve a two-electron process. The Cs⁺ complexes of these porphyrins, though formed in solution, do not exhibit any marked changes in the spectral features. This can be due to two reasons: (i) the effect of ion-dipole (of the ether oxygens) interactions are not transmitted to the porphyrin π -manifold because of large distance and/or absence of conjugation to the ring and (ii) the dimers of the *bis*

Cu(II)/Ni(II) SB porphyrins as a consequence of Cs^+ ion complexation do not possess the axial symmetry, and/or the distance between the two *bis*porphyrins in the dimer are very large.

4. Conclusions

It is shown that protonation of the Schiff-base derivatives of Ni(II) and Cu(II) porphyrins endowed with various amines, R-NH_2 , with varying R produces a red-shift of 40 nm in the *Q* bands of the porphyrin. The observed red-shift in these model compounds are analogous to the shift observed between the *in vivo* and *in vitro* chlorophyll molecules. This suggests that the structurally modified porphyrins form viable alternatives to the special-pair model of P680 in plant-bacterial photosynthetic systems. It is reasonable to assume that a protein residue can enter Schiff base formation with a formyl/keto group of the tetrapyrrole derivatives of P680. Protonation of this can lead to the observed red-shift in the primary donor in P680 relative to the isolated *in vitro* monomeric pigments. It is recognized that the plant pigments possess Mg ions in the macrocycle and the *in vitro* studies containing Mg ions are sensitive to demetallation on protonation. Moreover, the pigments bearing Mg are fluorescent while the Cu(II)/Ni(II) derivatives reported here are non-fluorescent. Interestingly, however, the observed two-electron oxidations in the protonated *bis*-Cu(II)SB porphyrins is encouraging in view of the recent studies in the search for multielectron catalytic systems of biological interest.

It is illustrated that the red-shift in the *Q* bands observed for the protonated SB derivatives essentially arise from the localized positive charge, $(-\text{CH}=\overset{+}{\text{N}}\text{HR})$, in the periphery of the macrocycle. Several lines of evidence have been presented for the non-interacting positive charge in these systems. We demonstrate here that the Schiff base formation need not necessarily arise from formyl porphyrins (where the formyl group is situated in one of the β -pyrrole rings) and an amine. Instead, a porphyrin amine, mono *p*-aminophenyl triphenyl porphyrin can be used for SB formation with benzaldehyde. The protonation of the latter leads to the red-shifts of the *Q* bands similar to that observed in the formyl-porphyrin Schiff bases (unpublished). This shows that the presence of a positive charge in any remote position can lead to the red shifts of the *Q* bands, arising from the perturbation/mixing of the π^* orbital of the substituent with the LUMO of the porphyrins.

Acknowledgements

This work is being supported by grants from the Department of Science and Technology, Government of India, New Delhi, and the Indian National Science Academy, New Delhi. The authors are thankful to these authorities for the funding.

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Interaction of rare earth metal ions with nucleosides—a study of binary and ternary systems in solution

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MS received 15 April 1986; revised 10 August 1987

Abstract. Studies on interaction of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Er(III) with inosine and xanthosine in a 1:1 ratio have been carried out by potentiometric equilibrium measurements at $35 \pm 0.1^\circ\text{C}$ and 0.1 M (KNO_3) ionic strength. Investigations were also made for the interaction of these metal ions and nucleosides with the biologically important secondary ligands glycine and histidine. These investigations were undertaken with a view to assess the influence of charge on the structure and stability of 1:1 metal-inosine/xanthosine systems.

Keywords. Lanthanide-nucleoside complexes; metal-inosine/xanthosine systems.

1. Introduction

Although the biological importance of nucleoside and nucleotide metal complexes has been recognised for long, we have only recently begun to understand the structural chemistry operating at biological sites where metal ions are found. A study of the specific mode and site of interaction of metal ions with nucleosides could provide useful information in understanding the nature of such interactions in biological systems. Such endeavours have yielded fruitful results earlier (Fritzsche 1970; Eichorn 1973; Rabindra Reddy *et al* 1976, 1978, 1979, 1983, 1984, 1985; Orenberg *et al* 1980; Rabindra Reddy and Harilatha Reddy 1983, 1985; Rabindra Reddy and Venugopal Reddy 1983; Bruce Martin 1985). However, data on complexes of metal ions of higher oxidation states are not available in the literature. Therefore, it was considered important to investigate the interaction of trivalent rare earth metal ions with nucleosides in both binary and ternary systems.

In the present paper, we report the stability constants of both binary and ternary complexes of inosine and xanthosine with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Er(III) and the biologically important secondary ligands, glycine and histidine. The interaction of these metal ions with secondary ligands has been attempted for the first time. The stabilities of trivalent metal-nucleoside

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complexes were found to be higher than those of the complexes of bivalent metal ions. The extra stabilization in the lanthanide metal complexes is attributed to the increased charge on the metal ions. We hope that this type of study will help in elucidating the various factors responsible for the stabilization of trivalent metal-nucleoside complexes in solution.

2. Experimental

Inosine, xanthosine, glycine and histidine were obtained from Sigma Chemical Company, St. Louis, USA. All the metal ions were of AnalaR grade and were used without further purification. For every titration fresh solid ligand was weighed out to avoid hydrolysis, which may take place when stock solutions are employed. The lighter rare earth metal ions were standardised volumetrically by titration with disodium salt of EDTA in the presence of a suitable indicator as described by Schwarzenbach (1957). Heavier rare earth metal ions were estimated gravimetrically (Kolthoft and Elving 1963). Carbonate-free sodium hydroxide was prepared by the method of Schwarzenbach and Biedermann (1948) and was standardised by titration with potassium hydrogen phthalate. The experimental method consisted of potentiometric titration of the metal ions and inosine, xanthosine, glycine and histidine in 1:1 and 1:1:1 ratios at $35 \pm 0.1^\circ\text{C}$ with standard sodium hydroxide solution. The experimental conditions maintained were the same as those described earlier (Rabindra Reddy *et al* 1984).

3. Calculations

The acid dissociation constants of ligands, inosine, xanthosine, histidine and glycine calculated by the usual algebraic method are presented in table 1.

Stability constants

The stability constants of 1:1 metal-inosine complexes were calculated using (1) (charges omitted for clarity).

$$K_{ML}^M = \frac{T_M - [M]}{[M][L]} \quad (1)$$

Table 1. Acid dissociation constants* of the ligands at $35 \pm 0.1^\circ\text{C}$ and $\mu = 0.1 \text{ M}$ (KNO_3).

Ligand	pK_a	pK_{2a}
Inosine	8.48 ± 0.02	—
Xanthosine	5.46 ± 0.02	9.70 ± 0.02
Glycine	2.33 ± 0.02	9.75 ± 0.02
Histidine	6.00 ± 0.04	9.00 ± 0.04

* From Rabindra Reddy *et al* 1985.

To calculate the stability constants of 1:1 protonated complexes of metal-xanthosine, equation (2) was employed.

$$K_{\text{MHL}}^{\text{M}} = \frac{T_{\text{M}} - [\text{HL}] X}{[\text{HL}]^2 \times [\text{H}^+]/K_{\text{a}} K_{2\text{a}}}, \quad (2)$$

where $X = ([\text{H}^+]^2/K_{\text{a}} K_{2\text{a}}) + ([\text{H}^+]/K_{\text{a}} K_{2\text{a}})$

and
$$[\text{HL}] = \frac{(1-a) T_{\text{L}} - [\text{H}^+] + [\text{OH}^-]}{[\text{H}^+]^2/K_{\text{a}} K_{2\text{a}}}.$$

Equation (2) was also used for obtaining the stability constants of 1:1 metal-glycine/histidine complexes.

For calculating the stability constants of ternary complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Er(III) with inosine (HL) and glycine/histidine (H_2A) in 1:1:1 ratio eq. (3) was employed.

$$K_{\text{MLA}}^{\text{M(HA)}} = \frac{T_{\text{M}} - [\text{M}]}{[\text{M}][\text{L}][\text{A}]} \quad (3)$$

The stability constants of the ternary complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Er(III) with xanthosine (H_2L) and histidine/glycine (H_2A) in a 1:1:1 ratio were calculated using

$$K_{\text{M(HL)(HA)}}^{\text{M}} = \frac{T_{\text{M}} - [\text{HL}] X}{[\text{HL}]^3 [\text{X}]^2} \quad (4)$$

This equation was described earlier (Rabindra Reddy and Harilatha Reddy 1985).

All calculations were made using the experimental data depicted in figures 1 and 2 on a Casio PB 100 personal computer employing suitable programmes.

4. Results

- (i) *Metal-inosine (1:1) system*: The formation constants for the normal 1:1 metal inosine complexes calculated using (1) are listed in table 2.
- (ii) *Metal-xanthosine (1:1) system*: The constants for the monoprotonated 1:1 metal-xanthosine complexes calculated using (2) are shown in table 2.
- (iii) *Metal-glycine and metal-histidine (1:1) systems*: The stability constants of 1:1 metal glycine/histidine complexes calculated using (2) are presented in table 2.
- (iv) *Metal-inosine-glycine/histidine (1:1:1) systems*: The stability constants of 1:1:1 metal-inosine-glycine/histidine complexes calculated using (3) are given in table 3.
- (v) *Metal-xanthosine-glycine/histidine (1:1:1) systems*: The interaction of rare earth metal ions with xanthosine and glycine/histidine in a 1:1:1 ratio resulted in the formation of diprotonated complexes. The constants were calculated using (4) and are also listed in table 3.

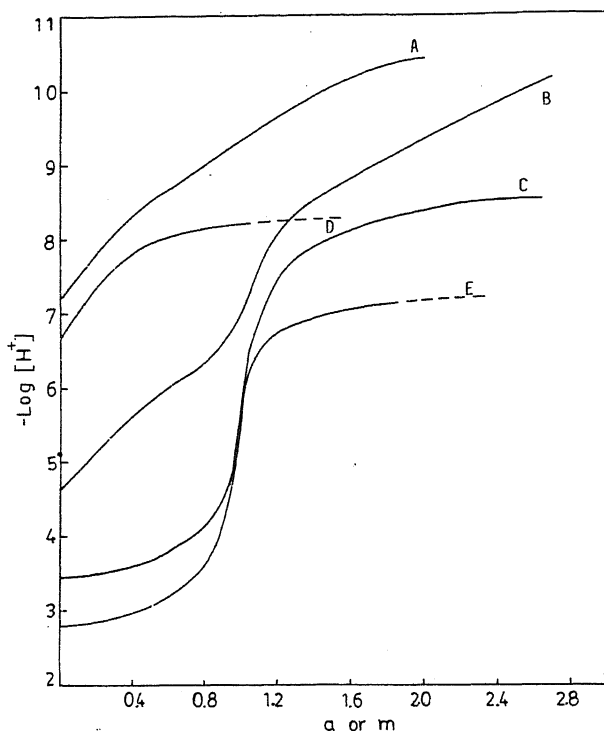


Figure 1. Potentiometric titration curves for La(III):inosine (1:1) and Dy(III):inosine:glycine (1:1:1) systems at 35°C and $\mu = 0.1$ M (KNO_3). a or m , moles of base added per mple of ligand for curves A, B, C; m , moles of base added per mole of metal ion for curves D and E. A, free inosine; B, free glycine; C, free histidine; D, La(III):inosine; E, Dy(III):inosine:glycine.

Table 2. Stability constants* for the interaction of rare earth metal ions with inosine, xanthosine, glycine and histidine in a 1:1 ratio at $35 \pm 0.1^\circ\text{C}$ and $\mu = 0.1$ M (KNO_3).

Metal ion (III)	Metal:inosine K_{ML}^{M}	Metal:xanthosine $K_{\text{M(HL)}}^{\text{M}}$	Metal:glycine $K_{\text{M(HA)}}^{\text{M}}$	Metal:histidine $K_{\text{M(HA)}}^{\text{M}}$
La	4.10	3.50	3.23	3.41
Pr	4.21	4.24	3.53	3.56
Nd	4.29	4.35	3.71	3.79
Sm	4.39	4.52	3.82	3.85
Gd	4.41	3.62	3.72	3.76
Dy	4.52	4.58	3.86	3.99
Er	4.71	4.63	3.93	4.06

* The constants are accurate to the extent of 0.06 log K units.

5. Discussion

The stability constants of metal-inosine and metal-xanthosine complexes decrease in the order: Er(III) > Dy(III) > Gd(III) > Sm(III) > Nd(III) > Pr(III) > La(III). The stability constants are inversely proportional to their ionic radii, as observed for a variety of ligands combining with the rare earth metals.

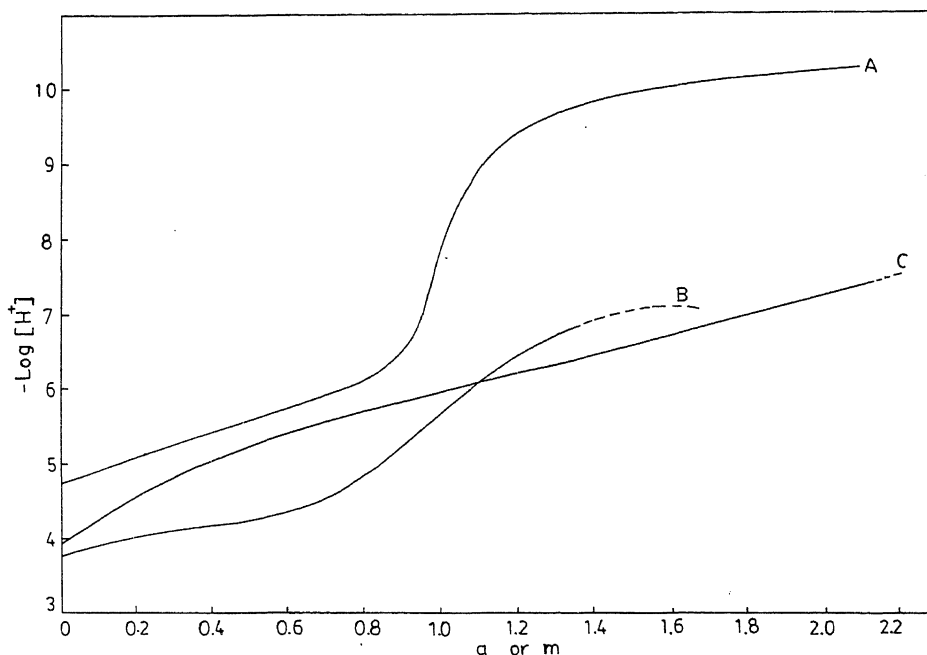


Figure 2. Potentiometric titration curves for Sm(III):xanthosine (1:1) and Er(III):xanthosine:histidine (1:1:1) at 35°C and 0.1 M (KNO₃) ionic strength. *a* or *m* = moles of base added per mole of ligand for curve A; *m*, moles of base added per mole of metal ion for curves B and C. A, free xanthosine; B, Sm(III):xanthosine (1:1); C, Er(III):xanthosine:histidine (1:1:1).

Table 3. Stability constants for the ternary rare earth chelates of inosine and xanthosine with glycine/histidine in a 1:1:1 ratio at 35 ± 0.1°C and $\mu = 0.1$ M (KNO₃).

Metal ion (III)	Metal:inosine:glycine $K_{M(A)}^{M(HA)}$	Metal:inosine:histidine $K_{M(A)}^{M(HA)}$	Metal:xantho:glycine $K_{M(HL)}^{M(HL)(HA)}$	Metal:xantho:histidine $K_{M(HL)}^{M(HL)(HA)}$	$\Delta \log K$	
					M: xantho: gly	M: xantho: histidine
Lr	9.32 ± 0.03	10.11 ± 0.05	5.00 ± 0.01	5.62 ± 0.06	-2.33	-1.89
Pr	9.51 ± 0.02	10.45 ± 0.06	5.10 ± 0.01	5.65 ± 0.06	-2.64	-2.04
Nd	9.90 ± 0.04	10.56 ± 0.02	5.16 ± 0.06	5.81 ± 0.09	-2.90	-2.22
Sm	10.22 ± 0.01	10.89 ± 0.05	5.28 ± 0.04	5.95 ± 0.08	-3.60	-2.30
Gd	10.52 ± 0.07	10.96 ± 0.02	5.36 ± 0.04	4.72 ± 0.08	-1.98	-3.04
Dy	10.58 ± 0.02	11.02 ± 0.04	5.42 ± 0.04	6.07 ± 0.04	-3.02	-2.39
Er	10.86 ± 0.04	11.09 ± 0.06	5.55 ± 0.01	6.49 ± 0.04	-3.01	-2.02

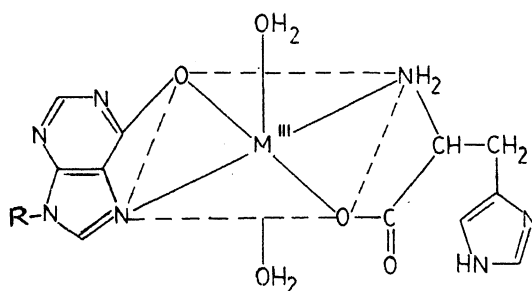
(Rabindra Reddy and Madhusudan Reddy 1985). It is of interest here to compare the stabilities of bivalent metal-inosine/xanthosine complex binary systems (Rabindra Reddy *et al* 1976, 1983) with those of the lanthanides. The lanthanone complexes are found to be more-stable than the bivalent metal complexes. The higher stability of the rare earth metal-nucleoside complexes can be explained on the basis of the differences in the charge on the metal ions. The rare earth metal

ions have smaller ionic radii as compared to bivalent metal ions because of their positive charge. This enables ligands to come closer to the central metal ion paving the way for better electrostatic attractions, which in turn result in stronger metal-ligand interactions. However, the types of complexes formed and the magnitudes of the stability constants suggest that the nature of bonding in both bivalent and trivalent metal complexes may be similar.

Interaction of the metal ions with glycine and histidine resulted in the formation of monoprotonated complexes. The closeness in the stabilities of 1:1 metal-glycine and metal-histidine complexes indicates that the mode of binding in metal-glycine and metal-histidine complexes is the same, i.e., histidine acts like glycine with the involvement of mixed N/O donor sites in metal coordination. This is different from the situation in transition metal complexes (Rabindra Reddy and Harilatha Reddy 1985) where histidine behaves as a terdentate ligand involving all its available donor sites in metal binding.

The ternary complexes of histidine in the case of both inosine and xanthosine are more stable than the ternary complexes of glycine. This is due to the fact that histidine, being an aromatic ligand, can participate in an additional interaction with inosine and xanthosine. This explanation is similar to that given for the transition metal complexes (Rabindra Reddy and Harilatha Reddy 1985). The $\Delta \log K$ values (the differences in the overall 1:1:1 ternary stability constants and the corresponding binary constants) for the xanthosine system are shown in table 3. The corresponding data for the inosine system could not be computed because of the formation of different types of complexes in both binary and ternary systems. The data for the xanthosine system show negative values. This suggests that protonated xanthosine complexes are less favoured. The normal complexes could not be observed because of the formation of precipitates. A comparison of even these negative $\Delta \log K$ values shows that histidine forms more stable complexes as compared to glycine even though the donor atoms involved in bonding are similar (N/O). This may be due to the aromaticity of histidine. Based on this observation we have proposed the tentative structure of metal-inosine-histidine (1:1:1) as shown in figure 3.

When the $\Delta \log K$ values of the ternary complexes of rare earth metal ions are compared with those of the corresponding ternary systems of transition metal ions,



R = Ribose

Figure 3. Tentative structure of M(III)-inosine-histidine (1:1:1) in solution.

we find that the rare earth mixed chelates are less stable than the transition metal complexes (Rabindra Reddy and Harilatha Reddy 1983, 1985). The lower stability of the ternary rare earth chelates may be due to the high stability of their 1:1 metal-inosine or 1:1 metal-xanthosine complexes. The higher stability of binary complexes of rare earth metal ions may disfavour the formation of ternary complexes in solution. A better understanding of these interactions can be obtained with a knowledge of thermodynamic parameters like ΔH_f^0 and ΔS_f^0 . Studies involving these parameters are presently being carried out.

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Synthesis and spectral characterization of dioxouranium(VI) complexes of salicylhydrazine and acetone salicylhydrazone

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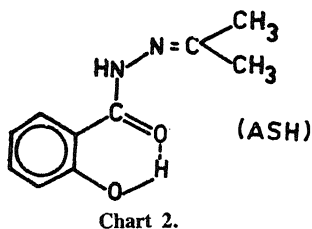
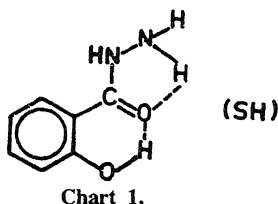
MS received 15 December 1986; revised 18 May 1987

Abstract. Dioxouranium(VI) complexes of the types UO_2LSO_4 and $\text{UO}_2\text{L}_2\text{SO}_4$ (where $\text{L} = \text{SH}$, ASH) have been prepared from reaction of uranyl sulphate with salicylhydrazine (SH) and acetone salicylhydrazone (ASH) and characterized by conventional chemical and physical measurements. Infrared and Raman spectra indicate that *mono*- and *bis*-complexes contain six- and seven-coordinate uranium atom respectively with all the ligand atoms arranged in an equatorial plane around the linear uranyl group. The infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) reveal that both SH and ASH act as neutral bidentate ligands coordinating through a carbonyl oxygen and primary amine/azomethine nitrogen atoms. The sulphato group coordinates to the uranyl ion as bidentate chelating ligand and terminal monodentate ligand in *mono*- and *bis*-complexes respectively.

Keywords. Dioxouranium complexes; infrared spectroscopy; Raman spectroscopy.

1. Introduction

Acylhydrazines (Zabalpurwala *et al* 1964; Sen Gupta and Dutta 1971, 1975; Alcock *et al* 1972; Iskander *et al* 1974; Biradar and Angadi 1976; Singh *et al* 1984b) and acylhydrazones (Narang and Aggarwal 1975; Aggarwal and Rao 1977, 1978; Pardhy *et al* 1979; Aggarwal *et al* 1981; Dutta and Sarkar 1981; Dutta and Hossain 1982; Johnson *et al* 1982; Patil *et al* 1982, 1983; Dutta and Das 1983; Singh *et al* 1984a; Lal *et al* 1986b) have been known to give stable complexes with transition and non-transition metal ions, yet their uranyl complexes have not been studied in detail (Zabalpurwala *et al* 1964; Aggarwal and Prasad 1971; Biradar and Angadi 1976; Paolucci *et al* 1985). The uranyl ion has strong affinity for oxygen donor ligands because of its hard acceptor properties (Sutton 1949; Cefola *et al* 1962; Pearson 1968; Khanolkar *et al* 1973; Deshpande *et al* 1977) and offers a large number of geometric structures usually hexa- to deca-coordinate (Zachariasen 1954; Wells 1966; Cattalini *et al* 1971; Ahuja and Singh 1973, 1977). In continuation of our recent study on the synthesis and structural assessment of dioxouranium(VI) complexes of aroylhydrazines and aroylhydrazones (Lal 1986; Lal *et al* 1986a), the present paper describes the preparation, characterization and infrared and Raman spectral features of the coordination compounds of the type UO_2LSO_4 and $\text{UO}_2\text{L}_2\text{SO}_4$ formed by the interaction of uranyl sulphate with SH and ASH which have been found to contain 6- and 7-coordinated uranium atom in *mono*- and *bis*-complexes respectively.



2. Experimental

2.1 Materials and measurements

Uranyl sulphate, ethyl salicylate, acetone and hydrazine hydrate used were from BDH, and were AR or equivalent grade. SH, m.p. 147 (lit. 148°C), was prepared by the method of Struve and Radehausen (1984). ASH, m.p. 206 (lit. 205°C), was prepared by condensing acetone with salicylhydrazine and recrystallized from ethanol (Ma and Tien 1953). Uranium in the complexes was estimated as U_3O_8 (Vogel 1973, p. 539). Sulphate was estimated as $BaSO_4$ (Vogel 1973, p. 462). Hydrazine was estimated volumetrically by KIO_3 after submitting the complexes to acid hydrolysis for ~ 4 h (Vogel 1973, p. 380). Nitrogen was analysed by microanalysis. Molecular weight of the complex $UO_2(ASH)SO_4$ was determined as a representative sample by Rast's method using diphenyl as a solvent (Mann and Saunders 1964). The molar conductance of the complexes at 10^{-3} M dilution in DMF was measured using an Elico conductivity bridge model CM-82T with a dip-type conductivity cell. IR spectra of the ligands and their complexes were recorded on Perkin-Elmer 577 spectrophotometer in CsI pellets in 4000–200 cm^{-1} region. Raman spectra were recorded on a Raman spectrophotometer (Ramalog 1403) in KBr by employing rotating sample technique to avoid decomposition of the sample.

2.2 Preparation of the complexes

The complexes were prepared by the following procedures.

(a) *Preparation of UO_2LSO_4 ($L = SH, ASH$) complexes:* The uranyl sulphate (50 ml, 0.01 M) in hot methanol was added into a solution of the ligand (110 ml, 0.01 M) in hot methanol and the mixture heated on a steam bath for about an hour with stirring. The precipitation of the complexes was effected by adding ether to the solution which was then concentrated to 90 ml and cooled to room temperature. The complexes were filtered by suction, washed with methanol and finally with ether and dried over anhydrous calcium chloride in a desiccator and then in an electric oven at 60–70°C.

(b) *Preparation of $UO_2L_2SO_4$ ($L = SH, ASH$) complexes:* The uranyl sulphate (1 g) was suspended in 100 ml hot ethanol. To this suspension, the ligand in ethanol (0.01 M) was added with continuous vigorous stirring maintaining the molar ratio at 1 : 2. The solution was refluxed for two hours and this precipitated the complex. The complex was filtered and washed with ethanol and ether and collected as above.

3. Results and discussion

The complexes isolated in the present study, their analytical data, melting point (decomposition point) and molar conductances are presented in table 1. Partial spectral data for the ligands and their complexes are presented in table 2.

The results of elemental analyses are consistent with 1 : 1 and 1 : 2 metal-to-ligand stoichiometry and accordingly these complexes have the general formula $[\text{UO}_2\text{LSO}_4]$ and $[\text{UO}_2\text{L}_2\text{SO}_4]$ (where $\text{L} = \text{SH}, \text{ASH}$). The molecular weight of the complex $\text{UO}_2(\text{ASH})\text{SO}_4$ determined as a representative sample (found, 538; calcd., 558) is compatible with the above stoichiometry. The complexes are sparingly soluble in ethanol and methanol but completely soluble in DMF only. The conductance measurements in DMF are in accord with the non-electrolytic nature (Geary 1971) of the complexes. Slightly higher values may be due to their partial solvolysis in the highly coordinating solvent DMF (Livingstone and Oluka 1978; Saha and Bhattacharya 1982).

Contributions due to the coordinated ligands were selected by comparing the IR spectra of the complexes with those of the free ligands and the residual features were assigned to the coordinated sulphato groups. Strong bands due to sulphato group are believed to superimpose and mask some of the ligand bands. SH shows absorption bands at 3333s, 3283s, 3151m while ASH shows a strong band at 3283 cm^{-1} and a strong broad band in the 3200–3000 cm^{-1} region (Mashima 1962). These bands are assigned to νNH and νOH vibrations. The medium to strong band present in the 2800–2700 cm^{-1} region of the IR spectra indicates the presence of strong intramolecular hydrogen bonding in the ligands.

The $\text{UO}_2(\text{SH})\text{SO}_4$ complex shows a strong broad band in the 3600–3400 cm^{-1} region and another strong broad band in the 3353–3000 cm^{-1} region with maximum absorption at 3290 cm^{-1} while the $\text{UO}_2(\text{SH})_2\text{SO}_4$ shows one strong broad band in the 3600–3400 cm^{-1} region and another very strong broad band in the 3350–2900 cm^{-1} region. The $\text{UO}_2(\text{ASH})\text{SO}_4$ complex shows a single medium broad band in the 3600–3100 cm^{-1} region with maximum absorption at 3475 cm^{-1} while the $\text{UO}_2(\text{ASH})\text{SO}_4$ complex shows a medium broad band in the 3600–3394 cm^{-1} and a very strong broad band in the 3354–3000 cm^{-1} region. The presence of only one band in the IR spectrum of $\text{UO}_2(\text{ASH})\text{SO}_4$ with maximum absorption at 3475 cm^{-1} suggests that the secondary amine group does not participate in bonding and $-\text{OH}$ group freed from intramolecular hydrogen bonding absorbs at higher frequency. The essentially different character of absorption bands in the 3600–2900 cm^{-1} region of IR spectra of $\text{UO}_2\text{L}_2\text{SO}_4$ (where $\text{L} = \text{SH}$ and ASH) complexes compared to those of UO_2LSO_4 (where $\text{L} = \text{SH}, \text{ASH}$) complexes may be attributed to the development of a new intramolecular hydrogen bonding between OH groups of the salicyl grouping of the two ligands coordinated to the uranyl ion.

The most outstanding feature of the IR spectra of the uranyl complexes studied here is observable in the 1700–1500 cm^{-1} region which contains bands due to $>\text{C}=\text{O}$, $>\text{C}=\text{N}$, $-\text{NH}_2$ and $\text{C}-\text{O}$ group frequencies. In the complexes, amide I band appearing at 1645 cm^{-1} and 1650 cm^{-1} and δNH_2 and $\nu\text{C}=\text{N}$ appearing at 1630 and 1620 cm^{-1} in uncoordinated SH and ASH respectively suffer marked negative shift and appear in the 1635–1630 and 1618–1600 cm^{-1} region respectively. The lowering of $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{N}/\delta\text{NH}_2$ bands is attributed to the drainage of

electron density from oxygen of $>C=O$ group and nitrogen of $>C=N$ or NH_2 group as a result of oxygen-to-metal and nitrogen-to-metal coordination (Zabalpurwala *et al* 1964; Paul and Chadha 1969; Sen Gupta and Dutta 1971, 1975; Alcock *et al* 1972; Iskandar *et al* 1974; Narang and Aggarwal 1975; Biradar and Angadi 1976; Aggarwal and Rao 1977, 1978; Pardhy *et al* 1979; Aggarwal *et al* 1981; Dutta and Sarkar 1981; Dutta and Hossain 1982; Johnson *et al* 1982; Patil *et al* 1982, 1983; Dutta and Das 1983; Singh *et al* 1984a, b; Woon *et al* 1985; Lal *et al* 1986b). The lowering in amide I, $\nu C=N$ and δNH_2 vibrations is of the magnitude expected for complexes in which the $>C=O$, $>C=N$, $-NH_2$ groups and negatively charged ligands (SO_4^{4-}) constitute the first coordination sphere around the uranyl group. The involvement of $>C=O$ group in coordination is also confirmed from the fact that the amide II band at 1585 cm^{-1} in SH and 1595 cm^{-1} in ASH also suffers a considerable negative shift and appears in the $1560\text{--}1550\text{ cm}^{-1}$ region as either medium band or strong band in the IR spectra of the complexes. The IR spectra of the uncoordinated SH and ASH show absorption band at 1525 cm^{-1} which is assigned to C–O (phenolic) stretching (Rastogi *et al* 1978). This band remains unaltered in position and intensity in the IR spectra of the complexes. Such a feature of this band clearly indicates the absence of interaction between $-OH$ of salicyl group and uranyl ion (Issa *et al* 1967).

In addition to the ligands and sulphato group bands, the rock salt region IR spectra of the uranyl complexes studied here show very strong broad absorption bands in the $922\text{--}915\text{ cm}^{-1}$ region. This band is assigned to asymmetric stretching vibration ν_3 of uranyl group. Complexes 1 and 3 show weak absorption bands at 842 and 850 cm^{-1} . The symmetric stretching vibration ν_1 is IR-forbidden. However, the forbidden vibrations may become allowed as a result of particular symmetry properties of the molecules. The absence of a strong band assignable to ν_1 implies that the linearity of the UO_2^{2+} group is maintained in these complexes. The Raman spectra of $UO_2(SH)SO_4$ and $UO_2(ASH)SO_4$ complexes were recorded as representative samples in the $900\text{--}800\text{ cm}^{-1}$ range and show a strong broad band centred at 855 and 852 cm^{-1} . The OUO bending vibration occurs as a medium to strong band in the $260\text{--}255\text{ cm}^{-1}$ region in the low frequency IR spectra of these complexes. The OUO bending mode in ASH complexes masks a weak ligand band at 255 cm^{-1} .

The UO_2LSO_4 ($L = SH$ and ASH) complexes show four bands at 1245 , 1190 , 1155 , 1100 and 1225 , 1190 , 1175 , 1155 cm^{-1} respectively masking ligand bands in the $1250\text{--}1100\text{ cm}^{-1}$ region. The strong broad band due to triply degenerate ν_3 mode in the ionic sulphate splits into three bands when sulphato group coordinates to the metal ions as a bidentate chelating ligand. Although most of the ligand absorption bands in the region $1250\text{--}1100\text{ cm}^{-1}$ are masked by strong absorption bands due to sulphato group, one absorption band due to ligand appears as strong as sulphato group absorption band in the IR spectra of these complexes and hence maintains its identity in the spectra. In view of the absence of isotopic substitution studies, it is difficult to assign unambiguously the absorption bands due to sulphato group and ligands definitely. The triply degenerate OSO bending mode ν_4 which occurs as a sharp well-defined band at 610 cm^{-1} in sulphates with T_d symmetry also splits up into its components at 660 , 640 , 590 cm^{-1} in the complex $UO_2(SH)SO_4$ and 650 , 600 , 585 cm^{-1} in the complex $UO_2(ASH)SO_4$ respectively. Moreover, the ν_1 band (IR-forbidden in the uncoordinated sulphato) appears at 1030 cm^{-1} as

either a strong or a very strong band. Besides ν_1 , ν_3 and ν_4 , the ν_2 mode is observed as either a strong or medium intensity band at 480 or 470 cm^{-1} in the low-frequency IR spectral region. The positions of the absorption bands due to sulphato group are consistent with those normally associated with chelating sulphato group (Nakamoto *et al* 1959; Barraclough and Tobe 1961; Baldwin 1963; Cotton and Wilkinson 1972).

The spectra of the $\text{UO}_2\text{L}_2\text{SO}_4$ ($\text{L} = \text{SH}$ or ASH)-type complexes are essentially different from those of UO_2LSO_4 ($\text{L} = \text{SH}$, ASH)-type complexes. In these complexes, the ν_1 and ν_2 appear as either a medium or strong band at 1030 and 1025, and 470 and 480 cm^{-1} respectively. The type of coordination of sulphato group is usually judged from the splitting of ν_3 and ν_4 into its components. In the present complexes, ν_3 mode is split into two strong broad bands (1225–1150 cm^{-1} and 1120–1080 cm^{-1} in complex $\text{UO}_2(\text{SH})_2\text{SO}_4$ and 1240–1170 cm^{-1} and 1140–1060 cm^{-1} in complex $\text{UO}_2(\text{ASH})_2\text{SO}_4$. Such a feature of the IR spectra of 1 : 2 complexes is characteristic of sulphato group in C_{3v} symmetry and suggests its monodentate coordination (Nakamoto 1978). The monodentate coordination of the sulphato group is also confirmed from the fact that the sharp well-defined band at 610 cm^{-1} due to triply degenerate ν_4 mode in ionic sulphate splits into a doublet at 630, 600 cm^{-1} in $\text{UO}_2(\text{SH})_2\text{SO}_4$ and at 640, 605 cm^{-1} in $\text{UO}_2(\text{ASH})_2\text{SO}_4$ complexes respectively.

Considering that SH and ASH act as bidentate chelating ligands and sulphato group as a bidentate chelating ligand in UO_2LSO_4 ($\text{L} = \text{SH}$, ASH)-type complexes and as a terminal monodentate ligand in $\text{UO}_2\text{L}_2\text{SO}_4$ ($\text{L} = \text{SH}$, ASH) complexes respectively, the complexes are tentatively assigned monomeric structures (charts 3 and 4) involving six- and seven-coordinated uranium atom in UO_2LSO_4 and $\text{UO}_2\text{L}_2\text{SO}_4$ complexes respectively with four and five ligand atoms arranged around the linear uranyl group.

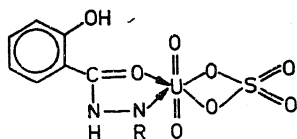


Chart 3

UO_2LSO_4 ; $\text{L} = \text{SH}$, ASH ;

$\text{R} = \text{H}_2(\text{SH})$, $= \text{C}(\text{CH}_3)_2(\text{ASH})$

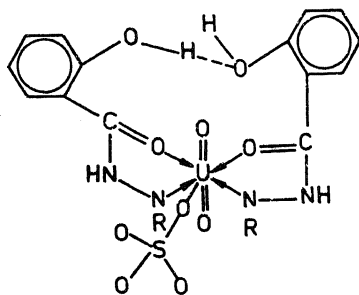


Chart 4

$\text{UO}_2\text{L}_2\text{SO}_4$; $\text{L} = \text{SH}$, ASH ;

$\text{R} = \text{H}_2(\text{SH})$, $= \text{C}(\text{CH}_3)_2(\text{ASH})$

Acknowledgements

The author is thankful to Prof. Saingenga for encouragement, to Dr D T Khathing, Regional Sophisticated Instrumentation Centre, NEHU, for nitrogen analysis and IR spectra and to Prof A L Verma, Department of Physics, NEHU, for Raman spectra.

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X-ray structure of dihydrazinium uranyl dioxalate monohydrate

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MS received 8 July 1987; revised 19 November 1987

Abstract. The crystal structure of dihydrazinium uranyl dioxalate monohydrate, $(\text{N}_2\text{H}_5)_2[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$, has been determined by x-ray diffraction. The structure was solved by heavy-atom method and refined to an R value of 0.059 using 2312 reflections. The N_2H_5^+ ions are not coordinated to the metal. In the anion $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$, the linear UO_2^{2+} group is coordinated by two chelating bidentate oxalate oxygens and a water oxygen. The coordination polyhedron around the uranium atom is an approximate pentagonal bipyramid.

Keywords. Hydrazinium uranyl oxalate; crystal structure; uranyl complex.

1. Introduction

The uranyl ion, UO_2^{2+} , the most stable species among uranium compounds present in nature, has a linear structure. In uranyl complexes, the ligands coordinate to the metal centre in a plane nearly perpendicular to the O-U-O axis as shown by the structures of uranyl systems containing a variety of ligands. In the coordination chemistry of UO_2^{2+} , the chelating ligand oxalate, in particular, has drawn special attention due to the fact that complexes of different types are formed depending upon the $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ mole ratio and the nature of oxalate coordination (Alcock 1973a, b, c; Jeyadevan and Chackraburthy 1972; Jeyadevan *et al* 1975; Dalley *et al* 1972; Niinisto *et al* 1978, 1979). An additional interesting feature of the ligand is that it has an unusually large bite distance of $\approx 2.7 \text{ \AA}$.

We have been interested in the interaction of the hydrazinium ion, N_2H_5^+ , with metal complexes containing various anionic ligands like sulphate (Govindarajan *et al* 1986a), oxalate (Gajapathy *et al* 1983) and hydrazine carboxylate (Ravindranathan and Patil 1985). Recently the structures of a hydrazinium uranyl oxalate complex, $(\text{N}_2\text{H}_5)_6[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]\cdot 2\text{H}_2\text{O}$ was reported (Govindarajan *et al* 1986b). This paper describes the structure of a related complex, $(\text{N}_2\text{H}_5)_2[(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ with a $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ (1:2) mol ratio.

2. Experimental

The complex was prepared by mixing aqueous solutions of uranyl nitrate hexahydrate (5.02 g, 10 mmol) and hydrazinium oxalate (3.08 g, 20 mmol) in the

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molar ratio of 1:2. Yellow acicular crystals appeared on slow evaporation. The composition of the crystals was fixed by the conventional analysis of hydrazine, oxalate and uranyl groups (Govindarajan *et al* 1986b) to be $(\text{H}_2\text{H}_5)_2\text{UO}_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}$. Analysis: hydrazine—observed 12%, required 12.07%; oxalate—observed 33%, required 33.2%; and uranium—observed 45.0%, required 44.9%.

3. X-ray crystallography

Crystal data: $\text{C}_4\text{H}_{12}\text{N}_4\text{O}_{11}\text{U}$, $M = 530$, monoclinic, space group $P2_1/n$, $a = 7.850(2)$, $b = 10.893(3)$, $c = 15.051(4)$ Å, $\beta = 100.96(2)^\circ$, $V = 1263.5$ Å³, $Z = 4$, $D_c = 2.78$ g cm⁻³, $F(000) = 976$, MoK_α radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo}-\text{K}_\alpha) = 165.06$ cm⁻¹, specimen dimensions: $0.25 \times 0.18 \times 0.1$ mm, $2\theta_{\text{max}} = 55^\circ$.

Unit cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles for 24 carefully selected and centred reflections on a CAD-4 automated diffractometer. Intensity data were collected in the $\omega/2\theta$ scan mode with a constant scan speed of 1° min^{-1} and scan width of $\theta = (0.75 + 0.45 \tan \theta)$. The intensities of three standards were monitored after every 3000 s and showed no systematic variations over the duration of the experiment. Of the 3512 reflections collected, 2312 were considered to be observed [$F_0 > 3 \sigma(F_0)$]. The data were corrected for Lorentz and polarization effects. An absorption correction was applied on the basis of the dimensions and face assignments (Sheldrik 1976).

The structure was solved by the heavy-atom method and refined using full-matrix least-squares method. Hydrogen atoms of the N_2H_5^+ groups could not be located. The final values of the discrepancy indices are:

$$R = \Sigma (|F_0| - |F_c|) / \Sigma F_0 = 0.059 \text{ and}$$

$$R^1 = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w|F_0|^2]^{1/2} = 0.057.$$

The weighting scheme used was $w = 2.32/\sigma^2(F) + 0.00047|F|^2$.

Computations were carried out on a DEC-10 computer. SHELX-76 (Sheldrik 1976) was used for structure solution and refinement. The curve for neutral scattering factors for U was taken from *International tables for x-ray crystallography* (1974). The scattering factors as available in SHELX-76 were used for all other atoms. Final atomic coordinates and equivalent isotropic temperature factors are listed in table 1, and bond parameters in table 2.

4. Results

The structure of $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ anion is shown in figure 1. The uranyl group is coordinated by four oxygen atoms of two chelating bidentate oxalate groups and a water oxygen atom. The coordination polyhedron is an approximate pentagonal bipyramid, with the metal being virtually in the plane of the pentagon.

The uranyl ion is linear with an O-U-O angle of $178.0(4)^\circ$ with the two U-O distances of 1.770(8) and 1.773(8) Å. In the equatorial plane, the U-O (water) bond

Table 1. Final fractional coordinates ($\times 10^5$ for U; $\times 10^4$ for the rest) and equivalent isotropic temperature factors ($\times 10^3$) with estimated standard deviations (e.s.d.s) in parentheses.

$$U_{\text{iso}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	U_{iso}
U	73047(5)	28190(4)	57268(2)	17.3(1)
O(1)	8023(10)	1417(7)	5252(5)	20.0(2)
O(2)	6585(12)	4194(8)	6166(6)	28.0(3)
O(3)	4440(12)	2153(8)	5159(6)	27.0(3)
O(4)	6101(11)	1553(9)	6738(5)	28.0(3)
O(5)	9359(13)	2423(8)	7094(6)	29.0(3)
O(6)	9989(10)	3819(7)	5783(5)	21.0(3)
O(7)	1986(11)	1231(8)	5388(6)	29.0(3)
O(8)	3917(13)	421(10)	7040(6)	41.0(3)
O(9)	12039(13)	2651(8)	7890(7)	32.0(3)
O(10)	12789(11)	4051(8)	6449(6)	30.0(3)
O(w)	6696(12)	3740(8)	4255(5)	27.0(3)
C(1)	3511(15)	1512(11)	5617(7)	21.0(3)
C(2)	4578(16)	1142(11)	6556(8)	23.0(3)
C(3)	10880(16)	2844(10)	7215(8)	21.0(3)
C(4)	11284(15)	3651(11)	6421(8)	22.0(3)
N(1)	2397(17)	3197(11)	3625(8)	34.0(4)
N(2)	700(16)	3337(12)	3849(8)	35.0(4)
N(3)	793(16)	635(11)	3055(8)	35.0(4)
N(4)	-359(13)	674(11)	3711(7)	28.0(3)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s. in parentheses.

U-O(1)	1.770(8)	U-O(6)	2.359(8)	C(2)-O(4)	1.257(14)	C(4)-O(6)	1.271(14)
U-O(2)	1.773(8)	U-O(w)	2.395(8)	C(2)-O(8)	1.249(15)	C(4)-O(10)	1.253(14)
U-O(3)	2.363(9)	C(1)-O(3)	1.298(14)	C(3)-O(5)	1.260(15)	N(1)-N(2)	1.444(16)
U-O(4)	2.379(8)	C(1)-O(7)	1.220(14)	C(3)-O(9)	1.246(15)	N(3)-N(4)	1.461(16)
U-O(5)	2.400(9)	C(1)-C(2)	1.552(16)	C(3)-C(4)	1.564(17)		
O(1)-U-O(2)	178.0(4)	O(2)-U-O(5)	92.4(4)	O(4)-U-O(6)	134.9(3)	O(4)-C(2)-C(1)	116(1)
O(1)-U-O(3)	87.4(3)	O(2)-U-O(6)	86.7(4)	O(4)-U-O(w)	143.2(3)	O(8)-C(2)-C(1)	119(1)
O(1)-U-O(4)	88.5(4)	O(2)-U-O(w)	88.3(4)	O(5)-U-O(6)	66.6(3)	O(4)-C(2)-O(8)	125(1)
O(1)-U-O(5)	89.1(3)	O(3)-U-O(4)	65.6(3)	O(5)-U-O(w)	148.4(3)	O(5)-C(3)-C(4)	115(1)
O(1)-U-O(6)	92.6(3)	O(3)-U-O(5)	133.9(3)	O(6)-U-O(w)	81.9(3)	O(9)-C(3)-C(4)	120(1)
O(1)-U-O(w)	89.8(3)	O(3)-U-O(6)	159.5(3)	O(3)-C(1)-C(2)	111(1)	O(5)-C(3)-O(9)	126(1)
O(2)-U-O(3)	92.6(4)	O(3)-U-O(w)	77.6(3)	O(7)-C(1)-C(2)	122(1)	O(6)-C(4)-C(3)	114(1)
O(2)-U-O(4)	93.3(4)	O(4)-U-O(5)	68.3(3)	O(3)-C(1)-O(7)	127(1)	O(10)-C(4)-C(3)	120(1)
						O(6)-C(4)-O(10)	126(1)

length is 2.395(9) Å, and the U-O (oxalate) distances vary from 2.359(8) to 2.400(9) Å, with an average value of 2.375 Å. These values are in good agreement with those observed for other UO_2^{2+} complexes of similar coordination (Alcock 1973c; Dalley *et al* 1972; Niinisto *et al* 1978, 1979). Both the oxalate groups, which bind the metal through 1,4-coordination, are virtually planar.

The N-N distances of 1.44(2) and 1.46(2) Å in the two crystallographically independent N_2H_5^+ ions are comparable to those found in other complexes (Gajapathy *et al* 1983; Prodic *et al* 1972; Bukovec and Golic 1976).

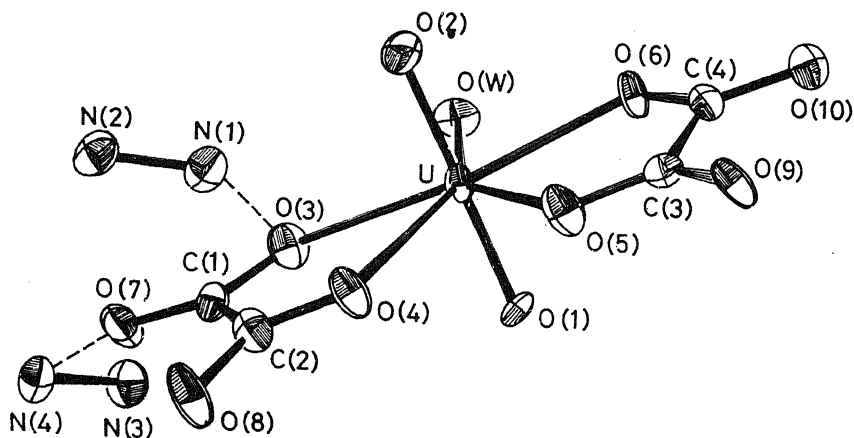


Figure 1. Structure of $(\text{N}_2\text{H}_5)_2[(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$. Broken lines indicate hydrogen bonds.

In the crystal, the discrete $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ ions are linked by hydrogen bonds. Both the free and coordinated oxygen atoms of $\text{C}_2\text{O}_4^{2-}$ act as acceptors. The coordinated water donates both its protons to the oxygen atoms of $\text{C}_2\text{O}_4^{2-}$ belonging to a neighbouring $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ moiety. The nitrogen atoms of the N_2H_5^+ ions are also involved in hydrogen bonds with the oxygen of oxalate groups.

5. Discussion

Depending upon the uranyl-oxalate ratio 1:1, 1:1.5, 1:2 or 1:3, complexes of the type: $\text{UO}_2\text{C}_2\text{O}_4$ (Jeyadevan and Chackraburthy 1972; $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]^{2-}$ (Jayadevan *et al* 1975; Alcock 1973c); $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2]^{2-}$ (Alcock 1973b); or $[(\text{UO}_2)(\text{C}_2\text{O}_4)_3]^{4-}$ (Alcock 1973a), respectively, are formed. The uranyl oxalate complexes with $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ mol ratios of 1:1 (Jeyadevan and Chackraburthy 1972), 1:1.5 (Alcock 1973c) and 1:2 (Alcock 1973b) containing NH_4^+ cation have five coordinated uranyl groups. On the other hand, $\text{K}_2[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]$ (Jeyadevan *et al* 1975) and $(\text{NH}_4)_4[(\text{UO}_2)(\text{C}_2\text{O}_4)_3]$ (Alcock 1973a) complexes having $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ ratios of 1:1.5 and 1:3 have six coordinated uranyl groups. The present structure may be compared with that of the related compound, $(\text{N}_2\text{H}_5)_6[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]\cdot 2\text{H}_2\text{O}$ (Govindarajan *et al* 1986b), a 1:2.5 uranyl oxalate complex, where the uranyl ions have similar pentagonal coordination of two bidentate chelating oxalate groups and one bridging oxalate oxygen replacing a water oxygen in the title compound. However, in the structure of the complex (Alcock 1973b) having the same mol ratio (1:2) as in the present case, but with a different cation, NH_4^+ , the uranyl ion is coordinated by the oxalate oxygens only and the bridging oxalate anions produce infinite chains of $[\text{UO}_2(\text{C}_2\text{O}_4)_2]_n^{2n-}$.

Unlike the cases of hydrazinium complexes of neodymium sulphate (Govindarajan *et al* 1986a) transition metal double sulphate and copper chloride, in both the hydrazinium uranyl oxalate complexes structurally characterised so far, the N_2H_5^+ remains uncoordinated. While this may be due to the availability of a sufficient

number of oxalate groups for coordination in the diuranyl pentaoxalate complex (Govindarajan *et al* 1986b), in the present case a water oxygen is preferred over N_2H_5^+ for completing the pentagonal coordination of UO_2^{2+} . The inability of N_2H_5^+ to bind the metal is, presumably, due to its poor ligating ability coupled with the geometrical restrictions in the uranyl coordination sphere arising from the chelation of rigid oxalate groups.

Acknowledgements

The authors are grateful to Dr. S Govindarajan for the preparation of the compound and Prof. H Manohar for useful suggestions.

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Electrochemical study of triphenyltin piperidyl dithiocarbamate

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MS received 13 April 1987; revised 10 August 1987

Abstract. The reduction of triphenyltin piperidyl dithiocarbamate in acetone has been investigated using d.c. polarography and cyclic voltammetry. Polarographic reduction yielded four well-defined waves, two of which were diffusion-controlled and two of which appear to represent adsorption processes. The cyclic voltammetric study yielded results in close agreement with the polarographic data. Results appear to indicate the release of the dithiocarbamate moiety, followed by reduction to form the triphenyltin radical, which undergoes dimerization, as well as reduction to the triphenyltin anion. For comparison, the polarographic reduction of triphenyltin chloride was investigated. A mechanism similar to that proposed by earlier authors for the polarographic behaviour of tributyltin oxide was found.

Keywords. Electrochemical behaviour; triphenyltin piperidyl dithiocarbamate; polarography; cyclic voltammetry.

1. Introduction

Apart from their importance as fungicides, catalysts and stabilisers, organotin compounds show complex, but interesting electrochemical behaviour. The earliest recorded work appears to be the polarographic reduction of diethyltin chloride by Riccoboni and Peboff (1949). Other early work on trialkyltin halides is that by Costa (1950), Toropova and Saikina (1953) and Saikina (1957).

More recently, Dessy *et al* (1966) reported an electrochemical study of organometallic derivatives of group IV elements, including diphenyltin and triphenyltin chlorides. These authors found that polarographically, Ph_3SnCl in dimethyloxyethane exhibited two well-defined waves at -1.6 V and -2.9 V versus the Ag/AgClO_4 reference electrode. The wave at -1.6 V was attributed to the formation of hexaphenylditin ($\text{Ph}_3\text{SnSnPh}_3$), while that at -2.9 V was regarded as due to the formation of Ph_3Sn^- directly without $\text{Ph}_3\text{SnSnPh}_3$ as an intermediate. More detailed investigations were reported by Fleet and Fouzder (1975) on trialkyl and triaryl tin compounds. Booth and Fleet (1970) investigated the electrochemical reduction of triphenyltin acetate and triphenyltin hydroxide in 50% ethanol using a

† For convenience, the more commonly used terminology of piperidyl dithiocarbamate is used throughout the paper, in place of (piperidine-1-carbodithioato) triphenyltin(IV).

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Hg pool anode and an SCE reference electrode. Three waves were obtained polarographically; however, a large maximum obscured the third wave. The second and third waves were said to be diffusion-controlled. It was claimed that waves I and II corresponded to the same electrode reaction and that wave I is an adsorption wave due to adsorption of the product from wave II onto the electrode surface. The mechanism suggested was the formation first of the triphenyltin radical ($\text{Ph}_3\text{Sn}\cdot$), which can undergo a further reduction in a 1-electron step to form Ph_3Sn^- . However, it was claimed that the radical formed in the first reduction can undergo a side reaction to produce hexaphenylditin, which is adsorbed onto the electrode surface and corresponded to wave I.

In later work, Fleet and Fouzder (1975) re-investigated the electrochemistry of two organotin compounds – triphenyltin acetate and tributyltin oxide (TBTO). For the latter compound in 50% ethanol, using a three-electrode cell arrangement and an SCE reference electrode, four well-defined waves were found. The first and third waves were said to be typical of an adsorption process, while waves II and IV were ascribed to normal reduction waves. These results were confirmed by cyclic voltammetric studies. The mechanism proposed is that the second wave represents the reduction of the TBTO to yield the tributyltin radical, which is adsorbed onto the electrode surface to give an adsorption prewave (wave I). The fourth wave corresponds to the reduction of the tributyltin radical to give Bu_3Sn^- , while the third wave is thought to be due to adsorption of the electrolysis product onto the Hg surface. These results are not, therefore, in exact agreement with those in the earlier publication by Booth and Fleet (1970). Other workers, Devaud (1966) and Mehner *et al* (1968), as a result of polarographic investigations on triphenyltin halides, proposed different mechanisms.

In the course of work on the use of a series of organotindithiocarbamates as fungicides (Chandra *et al* 1987), the electrochemical behaviour was examined. This paper reports the electrochemical behaviour of one of the series, viz., triphenyltin piperidyl dithiocarbamate, which is representative of the series. As a preliminary, the polarographic behaviour of the triphenyltin chloride was examined and the results are reported in this paper.

2. Experimental

2.1 Preparation of the organotin compounds

Triphenyltin chloride was obtained from Alfa Products and used without further purification.

Triphenyltin piperidyl dithiocarbamate: The sodium salt of piperidyl dithiocarbamate was prepared using the method of Gleu and Schwab (1950) and Magee (1973). To synthesise the triphenyltin derivative, 100 ml of A.R. acetone were taken in a reaction vessel and the temperature lowered to -30°C . From two separate dropping funnels, an acetone solution of 1.95 g (0.005 mol) of triphenyltrichloride and an acetone solution of an equimolar quantity of sodium piperidyl dithiocarbamate were added to the reaction vessel at the same rate with constant stirring over a period of $1-1\frac{1}{2}$ h. Stirring was continued for a further 2 h at -30°C . The mixture was quickly filtered, while still cold (3–5 min). The filtrate was placed

under vacuum (≈ 2 torr) and the acetone removed, while maintaining the temperature between 0 and 10°C . The product remaining was dissolved in sodium-dried diethylether and recrystallised by slow air evaporation. The white crystals obtained were collected and dried in vacuum. Analytical data: C 56.65% (56.58); H 4.73% (4.91); N 2.70% (2.75). Calculated values in parentheses.

2.2 Apparatus

All the electrochemical work was carried out on an AMEL 471 Multipolarographic Analyser jacketted to allow thermostating at $25 \pm 0.2^\circ\text{C}$. A three-electrode system was used in the closest and most favourable electrode configuration to minimize uncompensated i.r. potential. For the polarographic work, a dropping mercury electrode (DME) and a 15 cm coiled platinum wire served as the working electrode and the counter electrode, respectively. As reference electrode, the Ag/AgClO₄ (0.02 M), NaClO₄ (0.40 M) system was chosen. A silver spiral immersed in a solution of 0.02 M AgClO₄ and saturated with NaClO₄ was separated from a salt bridge (0.40 M NaClO₄) by means of a No. 2 sintered glass disc. The salt bridge in turn was separated from the solution under study by means of a No. 2 sintered glass disc.

2.3 Solvent system

A number of solvent systems were examined. These included DMSO, propylene carbonate, 50% ethanol and acetone. The latter was found to be the most suitable solvent electrochemically and for compound solubility. All subsequent work was therefore carried out in this solvent. The supporting electrolyte was NaClO₄ dissolved in acetone.

3. Results and discussion

3.1 D.C. polarography

Triphenyltin chloride (Ph₃SnCl): In acetone, Ph₃SnCl gives five waves, Wave 'I, a pre-wave, had all the characteristics of an anodic wave. Wave III was obscured by a large maximum, which was difficult to remove with surface active agent, Triton-X-100. Waves II and IV also tended to produce small maxima, which were easily removed by Triton-X-100. Because of the proximity of the anodic prewave 'I and wave I, it was not possible to determine the behaviour of the latter wave with changing concentration etc. Up to a concentration of 5×10^{-4} M, wave II showed dependence on concentration, after which the wave height reached a limiting value. Waves III and IV were also dependent on concentration over a wide range of concentration.

For waves II and IV, limiting current/ $h^{\frac{1}{2}}$ was constant indicating diffusion control. Because of the proximity of wave I to wave 'I and the persistent maximum on wave III, it was not possible to determine accurate $i_l/h^{\frac{1}{2}}$ values for these waves. For waves II and IV, half-wave potentials were constant over a range of concentration. The number of electrons transferred in the electrode processes for

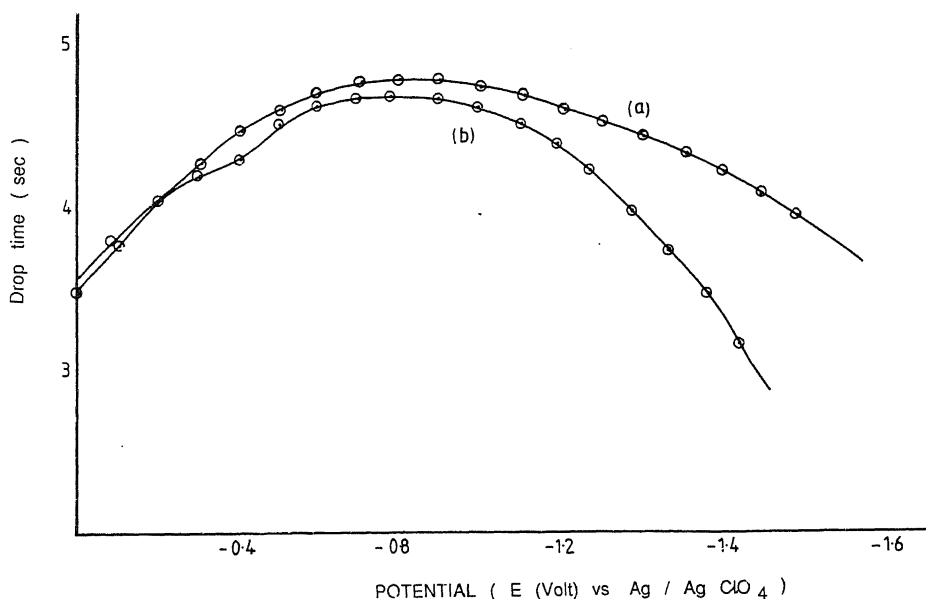


Figure 1. Electrocapillary curve for (a) 0.4 M NaClO₄ and (b) Ph₃SnCl (1 mM) in these waves was determined and found to be wave II, $n = 1$, and wave IV, $n = 1$, respectively.

The electrocapillary (drop-time) curves for Ph₃SnCl and the solvent-support system are shown in figure 1. The electrocapillary zero occurs at -0.8 V. Wave I for Ph₃SnCl occurs in the region -0.3 to -0.4 V: reduction, therefore, takes place at a negatively-charged electrode. Further, the drop-time curve for Ph₃SnCl indicates a lowering of surface tension in the potential regions -0.3 to -0.5 V and -1.6 V. It would appear that waves I and III are therefore due to adsorption processes. Based on these results, a mechanism similar to that proposed by Fleet and Fouzder (1975), who investigated the polarography and cyclic voltammetry of *bis*(tributyltin)oxide in 50% ethanol, can be assumed. Thus, wave I represents an adsorption wave, wave II, a normal reduction wave corresponding to the reduction of the triphenyltin cation, in a 1-electron transfer process, to the free radical (Ph₃Sn $\cdot$). Combination of the free radicals to form a dimer hexaphenylditin, which is adsorbed on the Hg surface could account for the adsorption wave III. The formation of hexaalkyl/hexaarylditin in the electroreduction of tri-substituted tin compounds has been confirmed (Devaud 1966). Finally, wave IV could represent a further reduction of the free radical (Ph₃Sn $\cdot$), to the anodic species Ph₃Sn $^-$.

3.2 The electrochemical behaviour of triphenyltin piperidyl dithiocarbamate

3.2a D.C. polarography: The piperidyl derivative of triphenyltin dithiocarbamate is of sufficient solubility in acetone for this solvent to act as a suitable system for the investigation. The same solvent-support system was used for Ph₃SnCl and the same reference electrode, viz., Ag/AgClO₄. Polarograms showed five well-defined waves labelled 'I, I, II, III, IV (figure 3), where 'I represent an anodic prewave. E values for the various waves were ≈ -0.29 (wave I), -0.7 (wave II), -0.95 (wave III) and -1.68 V (wave IV).

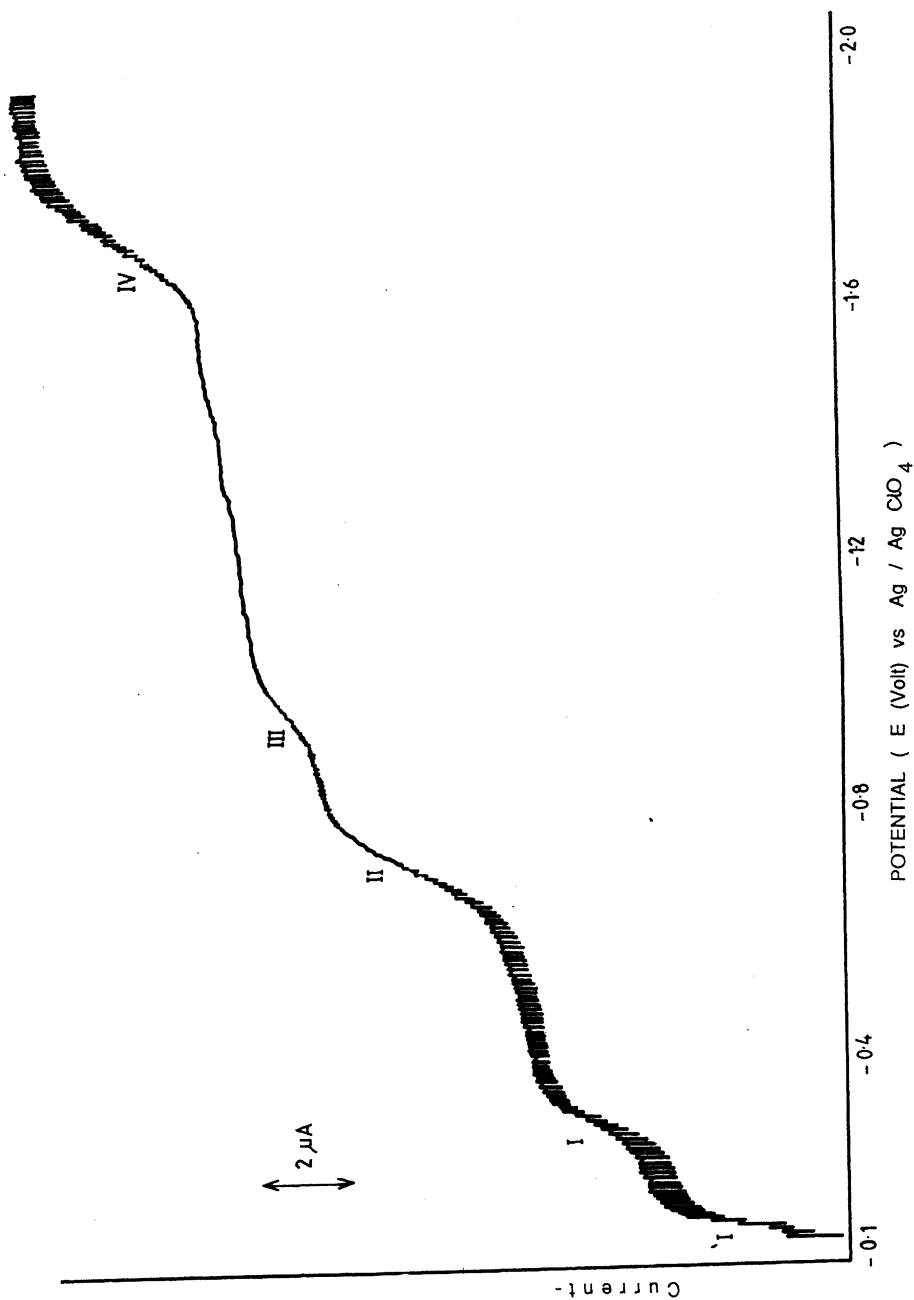


Figure 2. Polarogram of $\text{Ph}_3\text{Sn}(\text{dtc})(\text{pip})$ (1 mM) in acetone, 0.40 M NaClO_4 .
 $T = 25^\circ\text{C}$; $h = 68.0$ cm. 0.1% Triton X-100 added.

Up to a concentration of 1 mM, $E_{\frac{1}{2}}$ values for all waves were constant. Further, all waves showed a concentration-wave height dependence. For waves II and IV, limiting current/ $h^{\frac{1}{2}}$ was constant, indicating diffusion control. On the other hand, limiting current/ $h^{\frac{1}{2}}$ was not constant for waves I and III indicating departure from diffusion control and suggesting adsorption processes. The number of electrons transferred in the reduction processes producing wave II and wave IV was determined and found to be $n = 1$ and $n = 2$, respectively. The drop-time curve for $\text{Ph}_3\text{Sn}(\text{dtc})(\text{pip})$ and the solvent-support system are shown in figure 3 and indicates a lowering of surface tension in the potential region -0.3 to -0.5 and -0.7 to -0.9 V, which indicates adsorption processes in these regions, thus supporting the polarographic data.

3.2b Cyclic voltammetry: The cyclic voltammogram of $\text{Ph}_3\text{Sn}(\text{dtc})(\text{pip})$ in acetone at a scan rate of 200 mV/sec with Ag/AgClO_4 as reference electrode is shown in figure 4. The voltammogram is complex and consists of twelve peaks, seven cathodic and five anodic. The cathodic waves are labelled I_c , I_c' , II_c , III_c , III_c' and IV_c , where waves denoted by superscripts define the position of additional waves with respect to what are considered main waves. Corresponding anodic waves are denoted by a subscript 'a' e.g., I_a .

Waves I_c and I_a are due to the adsorption/desorption of a product of the reaction or the compound and appear to correspond to polarographic wave I.

Wave II_c : In agreement with the results of polarography, cyclic voltammetry indicates that this wave is a quasi-reversible or reversible, diffusion-controlled

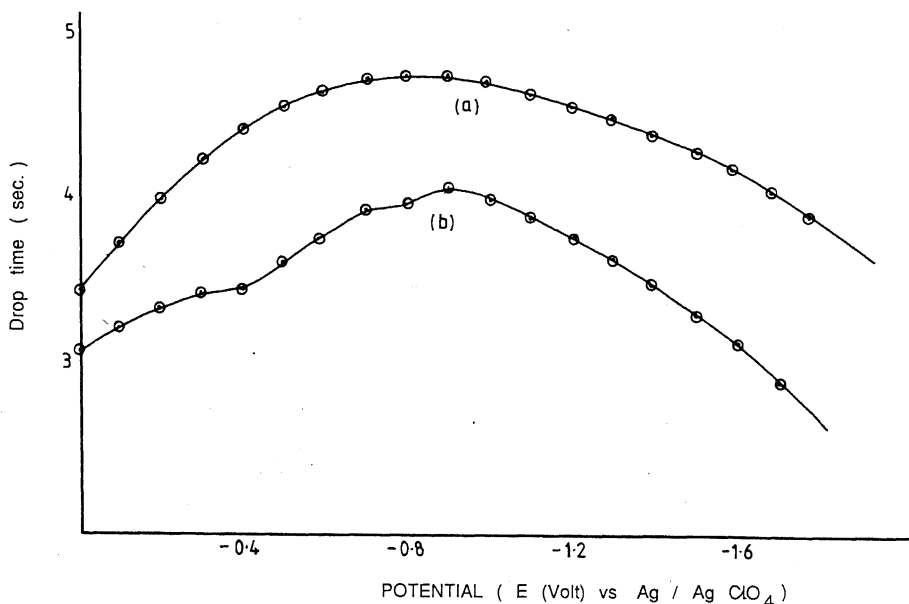


Figure 3. Electrocapillary curve for (a) 0.40 M NaClO_4 , (b) $\text{Ph}_3\text{Sn}(\text{dtc})(\text{pip})$ (1.00 mM) in acetone. $T = 25^\circ\text{C}$; $h = 68.0$ cm.

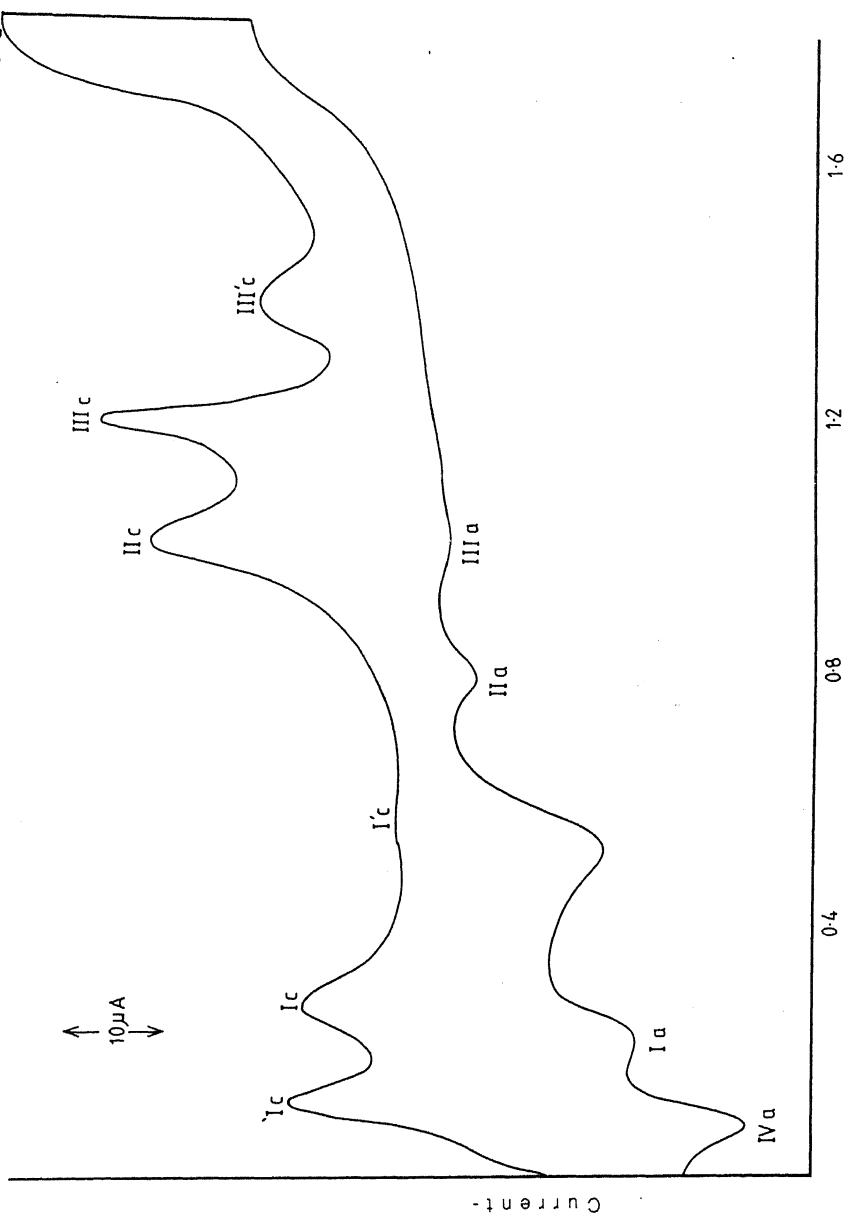


Figure 4. Cyclic voltammogram of $\text{Ph}_3\text{Sn}(\text{dte})(\text{pip})$ (1.00 mM) in acetone with 0.40 M NaClO_4 and 0.1% Triton X-100. $T = 25^\circ\text{C}$.

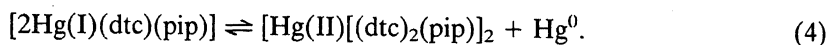
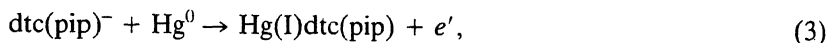
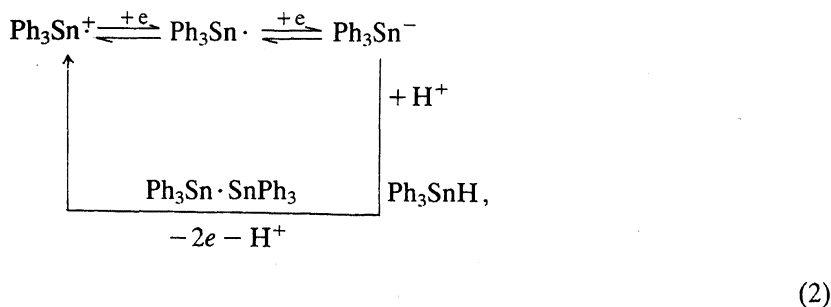
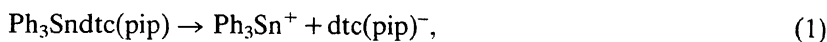
process. This is shown by $\Delta Ep[Ep_a - Ep_c]$ which is much greater than expected for a reversible process and increases with increasing scan rate. Diffusion control is indicated by the constancy of $ip_c(\text{plane})/\nu^{1/2}$ over a wide range of scan rates. An increase of ip_a/ip_c with increasing scan rate also indicates increasing irreversibility. Wave II_a is the corresponding anodic wave.

Wave III_c : This has the characteristics of an adsorption wave. $ip_c(\text{plane})\nu^{1/2}$ is dependent on scan rate. This adsorption wave is produced by adsorption of the dimer hexaphenylditin resulting from the combination of $\text{Ph}_3\text{Sn}\cdot$ radicals. Wave III_a is the peak due to the desorption of the species.

Wave IV_c : This was found to be a normal reduction wave. $ip_c(\text{plane})\nu^{1/2}$ was constant over a range of scan rates. It represents the reduction of the free radical, $\text{Ph}_3\text{Sn}\cdot$ to the anion Ph_3Sn^- . It is possible that the wave labelled IV_a represent the oxidation of Ph_3Sn^- back to Ph_3Sn^+ .

Waves I_c' and III_c' : In all the voltammograms run, these two peaks were present. I_c' occurs in the region around -0.55 V and III_c' around -1.37 volts. Earlier work in this laboratory by Ahmad & Magee (1979) on the electrochemical behaviour of metal dithiocarbamates showed that waves of this type and in the same regions were due to the release of dithiocarbamate ligand from the metal complex. On this basis, the wave I_c' could be due to the reduction of $\text{Hg(I)}-[\text{dtc}(\text{pip})]$, $\text{Hg(I)}[\text{dtc}(\text{pip})] + e' \rightarrow \text{Hg}^0 + \text{dtc}(\text{pip})$, following a chemical reaction $\text{Hg(II)}[(\text{dtc})_2\text{pip}]_2 + \text{Hg}^0 \rightarrow 2 \text{Hg(I)}[(\text{dtc})(\text{pip})]$. Wave III_c' may then be due to the fact that the reaction $\text{Hg(II)}[(\text{dtc})\text{pip}]_2 + \text{Hg}^0 \rightarrow 2[\text{Hgh(I)}(\text{dtc})(\text{pip})]$ does not go to completion, leaving part of the Hg(II) complex to be reduced at the more negative potential, i.e., -1.37 V. As there is no free ligand present in the original solution, the free ligand must have arisen by release from the $\text{Ph}_3\text{Sn}(\text{dtc})\text{pip}$ complex.

From the results obtained using polarography and cyclic voltammetry, it would appear that the mechanism of reduction might be proposed as follows:



The presence of the dithiocarbamate moiety as part of the complex makes the reduction of $\text{Ph}_3\text{Sndtc}(\text{pip})$ more complicated than the reduction of Ph_3SnCl . It

would appear that the difference in the mechanism of reduction of the two species is due to the release of the dithiocarbamate ligand (1), which then is able to react with mercury (3). Following this chemical reaction (4), the resulting product Hg(I)dtc(pip) is reduced. However, it is possible that the chemical reaction does not go to completion leaving the unchanged portion, i.e., Hg(II)[dtpip]_2 to be reduced at the more negative potential.

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A new synthesis of ($\pm$) and (+)-2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindenenes

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MS received 30 September 1987

Abstract. A new method for the preparation of the synthon ($\pm$)-2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindene (1,a) for the total synthesis of steroids in both ($\pm$) and (+) forms, starting from the known β -ketoester, ($\pm$)-methyl 1 β -*t*-butoxy-5,6,7,7a-tetrahydro-7a β -methyl-5-keto-4-indancarboxylate (2,a) has been described. An alternative route to (1,a) has been investigated. Although the compound, ($\pm$)-1 β -hydroxy-5,6,7,7a-tetrahydro-7a β -methyl-5-keto-4-methoxymethylindan (2,b) could not be prepared, interesting pathways leading to two unexpected products, ($\pm$)-5,6,7,7a-tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione and ($\pm$)-2,6-diketo-3-methyltricyclo-(5,2,1,0)decan-8-ol (3 and 4), were encountered during an attempted annelation reaction of the ketone, N-diethylamino-5-methoxypentan-3-one (6), with 2-methylcyclopentan-1,3-dione (5). Trapping of the intermediate, ($\pm$)-3a,4,5,6,7,7a-hexahydro-3a-hydroxy-4-methylene-7a-methylindene-1,5-dione (7), through the formation of the adduct, ($\pm$)-3a,4,5,6,7,7a-hexahydro-3a-hydroxy-4-(1',3'-diketo-2'-methylcyclopentano-2'-methylene)-7a-methylindene-1,5-dione (8), established the mechanism of the formation of the products (3 and 4).

Keywords. New synthesis; racemic and asymmetric synthesis; steroid synthone.

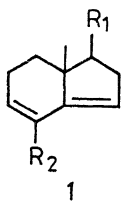
1. Introduction

The syntheses of ($\pm$) and (+)-2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindenenes (1,a) were reported earlier by us (Banerjee *et al* 1976, 1983), the yield in the last oxidation step being moderate and inconsistent, depending upon the brand of the reagent used. This prompted us to look for alternative routes.

2. New synthesis of ($\pm$) and (+)-2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindenenes

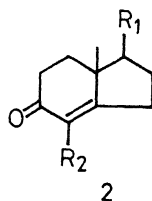
2.1 Synthesis of ($\pm$)-2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindene

Our starting material of choice for this synthesis was the diketoester (9, b or c), which has been earlier prepared by Collins and Tomkins (1977) and Ellis *et al* (1974). With the view to improving upon the yields obtained by the above workers, we utilized the β -ketoacid (2, c), prepared by Micheli *et al* (1975) from the enedione (10) which was prepared earlier by Boyce and Whitehurst (1959) in 70%



a, $R_1 = \text{OH}$; $R_2 = \text{CHO}$

b, $R_1 = \text{O}^+$; $R_2 = \text{CHO}$



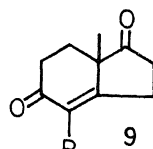
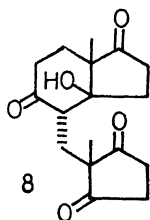
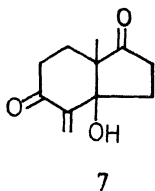
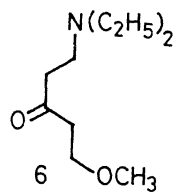
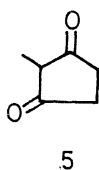
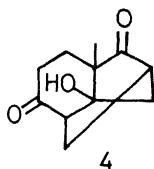
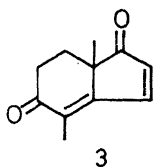
a, $R_1 = \text{O}^+$; $R_2 = \text{CO}_2\text{CH}_3$

b, $R_1 = \text{OH}$; $R_2 = \text{CH}_2\text{OCH}_3$

c, $R_1 = \text{O}^+$; $R_2 = \text{CO}_2\text{H}$

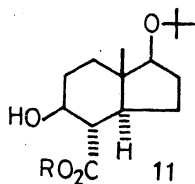
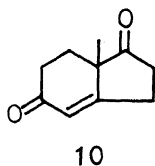
d, $R_1 = \text{OH}$; $R_2 = \text{H}$

e, $R_1 = \text{O}^+$; $R_2 = \text{H}$



a, $R = \text{CO}_2\text{H}$; b, $R = \text{CO}_2\text{CH}_3$

c, $R = \text{CO}_2\text{C}_2\text{H}_5$; d, $R = \text{CH}_3$



a, $R = \text{H}$

b, $R = \text{CH}_3$

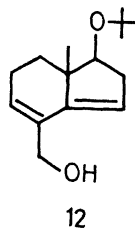


Chart 1.

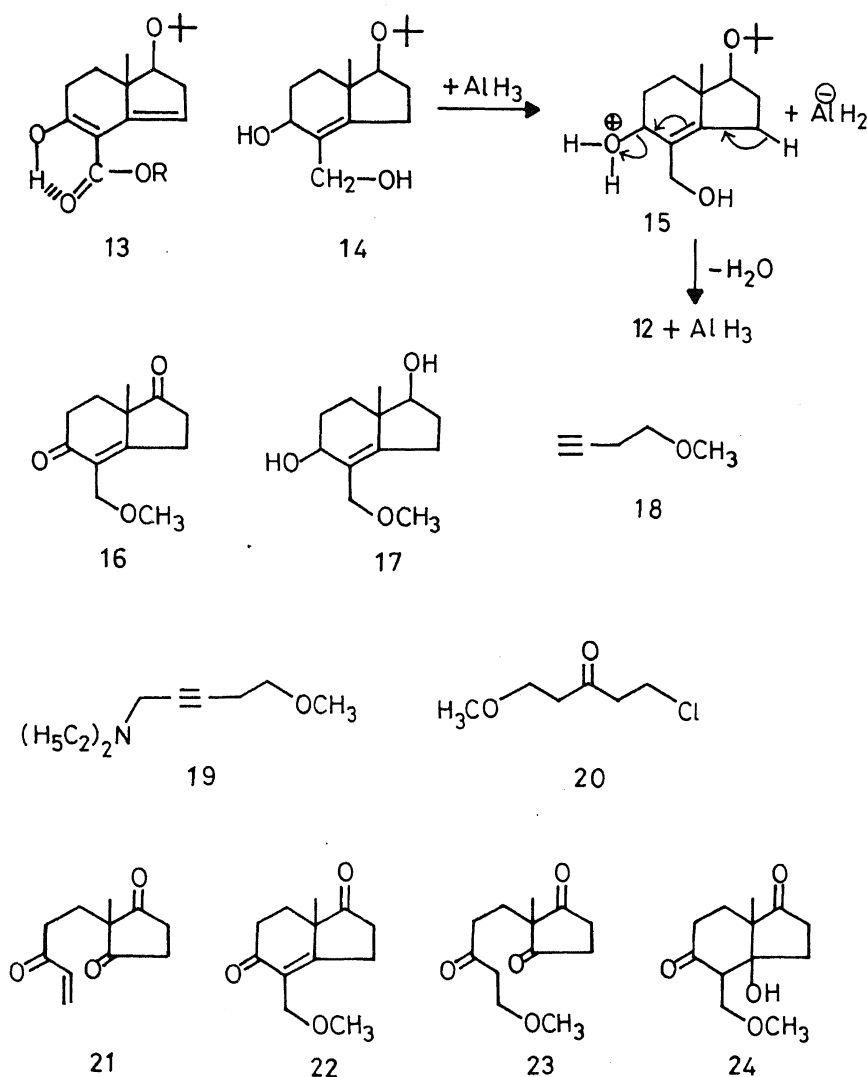


Chart 2.

yield. By adopting a modified one-step procedure of Zoretic *et al* (1976), we could obtain the enedione (10) in 90% yield. Following Micheli's method of selective reduction of the enedione (10) to the ketol (2, d), and subsequent treatment of the latter with isobutylene phosphoric acid-borontrifluoride etherate, afforded the *t*-butyl ether (2, e) in almost quantitative yield. The compound (2, e) was converted to the β -ketoacid (2, c) by treatment with methylmagnesiumcarbonate (MMC) (Balasubrahmanyam and Balasubramanian 1973) in 63% yield. Sodium borohydride reduction of the unsaturated ketoacid (2, c) and its ester (2, a) furnished the saturated hydroxyacid (11, a) and its ester (11, b) by the conjugate hydride addition followed by the reduction of the keto group in accordance with earlier observations (Nystron and Brown 1947; Hochstein and Brown 1948; Hochstein 1949; Dorrow

et al 1950; Bates *et al* 1954). The configuration assigned to 11, a and b, was proved by direct comparison with authentic samples prepared by the method of Baggiolini *et al* (1982).

Lithium aluminium hydride reduction of the acid (2, c) or its ester (2, a) afforded the diene alcohol (12). This obviously happened by the preferential reduction of the ester function, presumably due to the predominant existence of 2, c and a, as their enolates (13), followed by the reduction of the keto group to give the unsaturated diol (14) which underwent acid-catalysed allylic dehydration giving the dienol (12).

Aluminium hydride, derived from lithium aluminium hydride and aluminium chloride and known to reduce an unsaturated carbonyl without attacking the ethylenic linkage under mild conditions, reduced the unsaturated ketoester (2, a) to the dienol (12) in 95% yield; the probable mechanism, as schematically represented, appears to be an initial attack of the Lewis acid, aluminium hydride, on the secondary hydroxyl of 14 to form the oxycarbonium cation (15) and AlH_2 , followed by the splitting of a water molecule and proton to yield the dienol (12) with the regeneration of aluminium hydride. The same mechanism is supposed to be operative in the case of lithium aluminium hydride reduction.

The best yield (> 80%) of the *t*-butoxyaldehyde (1, b) was obtained when the dienol (12) was oxidized with active manganese dioxide (Attenburrow *et al* 1952) or with dimethyl sulphoxide-oxalyl chloride (Swern oxidation) (Mancuso *et al* 1978). Acidic removal of the *t*-butoxy group furnished the ($\pm$) hydroxy aldehyde (1, a).

2.2 Synthesis of (+)-2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindene

For our present synthesis of the (+)-hydroxy aldehyde (1, a), we started with the (+)-enedione (10), prepared by the recently reported procedure of Hajos and Parrish (1985), which was converted to the (+)- β -ketoacid (2, c) by our method for the preparation of ($\pm$)-2, c. The (+)-methyl ester (2, a) was then converted to the (+)-hydroxy aldehyde (1, a) by the reduction of the former with aluminium hydride, followed by the allylic oxidation of the resulting (+)-dienol (12).

3. Investigation of another route for the synthesis of ($\pm$)-2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindene

3.1 Attempted preparation of (+)-5,6,7,7a-tetrahydro-4-methoxymethyl-7a β -methylindan-1,5-dione

In our alternative new synthesis of the ($\pm$)-hydroxy aldehyde (1, a) we envisaged its preparation from the enedione ether (16) by its reduction to the enediol ether (17), followed by facile allylic dehydration, ether cleavage and oxidation. We intended to prepare 16 by the annelation of the dione (5) with the amino keto ether (6). The Mannich base (19), prepared from 2-methoxyethylacetylene (18), on hydration with mercuric sulphate and sulphuric acid gave a maximum yield of 25% of 6. Later, the compound (6) could be prepared in an overall yield of 56%, when the chloro methoxy ketone (20), prepared in 68% yield from 3-methoxypropionyl chloride, aluminium chloride and ethylene, was interacted with diethylamine. The annelation reaction between the amino ketone (6) and the dione (5), carried out

following Banerjee's procedure (Banerjee *et al* 1976), or by refluxing in xylene with PTS, gave a product which on purification by chromatography furnished a less polar compound, proved to be the dienedione (3) from its spectral data, and a more polar compound which was found to be 2,6-diketo-3-methyl-tricyclo[5,2,1,0]decan-8-ol (4), earlier reported by Danishefsky and Migdalof (1969) during the base catalysed cyclization of the vinyl triketone (21). The structure of the dienedione (3) was confirmed by hydrogenating it to the known enedione (9d). The compound (4), obtained in our annelation reaction, might have been formed from the vinyl triketone of Danishefsky and Migdalof during the base catalysed cyclization of the vinyl triketone (21). The structure of the dienedione (3) was confirmed by hydrogenating it to the known enedione (9d). The compound (4), obtained in our annelation reaction, might have been formed from the vinyl triketone of Danishefsky (1969), resulting by the elimination of methanol from the initially formed methoxy triketone (23). The compound (23), prepared independently, furnished the keto alcohol (4) by treatment with pyridine-benzene.

The cyclization of the methoxy triketone (23), as well as attempted annelations of the dione (5) with different annelating agents under various conditions failed to form 22. This led to the conclusion that the base-induced methanol elimination in the intermediate aldol (24), derived from 23, was more facile than dehydration to 22. The aforementioned methanol elimination formed the unsaturated hydroxy-enone (7) which by dehydration and isomerization finally gave the dienone (3). We could prove that this was indeed the pathway followed by trapping the postulated intermediate (7) by carrying out the well-known (Kuo *et al* 1965) self-catalysed annelation reaction of the acidic dione (5), used in excess, with the methoxy triketone (23) and isolating the expected adduct (8) formed by the addition of 5 to 7.

4. Experimental

All melting points (hot stage) and boiling points are uncorrected. All recorded temperatures are on the Celsius scale. Only one enantiomer of a racemic pair has been displayed in the charts. UV spectra were recorded in 95% ethanol on a Shimadzu UV-190 double beam spectrophotometer. IR spectra were taken on a Perkin-Elmer model 781 spectrophotometer. NMR spectra were recorded on a Varian T60, Varian HA-100, Jeol Fx 900 or Bruker WH-270 NMR spectrophotometer. Chemical shifts were quoted relative to TMS ($\delta = 0$ ppm) as internal standard. Mass spectra were recorded on a Jeol MS-DX 303 with a built-in direct inlet system. All organic extracts were dried over anhydrous sodium sulphate. Analytical and preparative layer chromatography were carried out using silica gel supplied by BDH (Bombay) or Acme Synthetic Chemicals (Bombay). For column chromatography Acme Silica gel or BDH neutral alumina was used.

4.1 ($\pm$)-7,7a-Dihydro-7a β -methyl-1,5(6H)-indandione (10)

A mixture of 2-chloroethyl methyl ketone (106 g, 1 mol) and the dione (5) (75 g, 0.67 mol) in water (600 ml) was stirred for 4 h and then heated under reflux with stirring for 16 h. The mixture was extracted with chloroform and the organic layer washed successively with water, aq. NaHCO_3 , water and brine. Removal of the

solvent and distillation of the residue afforded the dione (10) (148 g, 90%); IR (neat): $\nu_{\max}$ 1670, 1740 cm^{-1} ; ^1H NMR (CCl_4) δ 1.28 (s, 3H, CH_3), 1.7–3.1 (m, 8H, methylene), 5.78 (bs, 1H, vinylic).

4.2 ($\pm$)-7 α β -Methyl-7,7a-dihydro-1 β -hydroxy-5(6H)-indanone, (2, d)

To a chilled solution (-10°) of the indandione (10) (80 g, 0.24 mol) in ethanol (400 ml) was added NaBH_4 (5 g, 0.13 mol) in ethanol at a rate to maintain the internal temperature between -5 and -10° . The reaction mixture was then allowed to warm up to $+5^\circ$ and then cooled again to -10° and the pH adjusted between 5 and 7 by the addition of 2N HCl, the dark brown solution turning orange. The solvent was removed under vacuum (45°) and the residue was extracted with ethyl acetate. The residue, after removal of the ethyl acetate and purification by column chromatography (silica gel, CHCl_3), afforded the indanone (2, d) (78 g, 96%); IR (neat): $\nu_{\max}$ 3400, 1660 cm^{-1} .

4.3 ($\pm$)-1 β -t-Butoxy-7 α β -methyl-7,7a-dihydro-5(6H)-indanone, (2, e)

This compound was prepared following the method of Micheli *et al* (1975). Thus from the indanone (2, d) (40 g), $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (10 ml), H_3PO_4 (4.2 ml, 47% solution), dichloromethane (400 ml) and liquid isobutylene (200 ml), there was obtained the *t*-butyl ether (2, e) (50 g, 95%). The product, on purification by column chromatography (silica gel, ethyl acetate-hexane, 1:4), melted at 60 – 61° (reported 62 – 65°); IR (neat): $\nu_{\max}$ 1665 cm^{-1} ; ^1H NMR (CCl_4) δ 1.02 (s, 3H, CH_3), 1.04 [s, 9H, $\text{C}(\text{CH}_3)_3$], 1.8–2.9 (m, 8H, methylene), 3.58 (dd, $J = 8$ Hz, 1H, $\text{CH} = 0$), 5.56 (t, $J = 2$ Hz, 1H, vinylic).

4.4 ($\pm$)-5,6,7,7a-Tetrahydro-1 β -t-butoxy-7 α β -methyl-5-keto-4-indancarboxylic acid, (2, c)

A mixture of *t*-butyl ether (2, c) (50 g, 0.23 mol) and MMC in dimethylformamide (335 ml) was heated in a preheated (125°) oil bath with stirring under N_2 for 2 h, the internal temperature being maintained at 115° . The solution was cooled and poured into ice and conc. HCl. The aqueous phase was extracted with benzene and the organic phase with 15% aq. Na_2CO_3 . Acidification of the basic solution, followed by extraction with benzene and removal of the solvent in the vacuum (45°), gave a yellowish brown oily compound (35 g) which solidified on standing; crystallization from chloroform-hexane furnished the carboxylic acid (2, c) (26.5 g, 44%) as yellow crystals, m.p. 105° (reported 103 – 109°), IR (CHCl_3) $\nu_{\max}$ 1600, 1620, 1735 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.2 [(s, 12H, CH_3 , $\text{C}(\text{CH}_3)_3$), 1.4–2.8 (m, methylene), 3.62 (dd, $J = 8$ Hz, 1H, $\text{CH}-\text{O}$), 11.9 (bs, 1H, CO_2H).

Removal of the solvent from the neutral fraction gave the starting compound (15 g), the yield based on the recovery being 63%.

4.5 ($\pm$)-1 β -t-Butoxy-7 α β -methyl-3 $\alpha\alpha$,4 β ,5,6,7,7a-hexahydro-5 β -hydroxy-4 α -indancarboxylic acid, (11, a)

To a cooled and stirred solution of the carboxylic acid (2, c) (1.2 g, 4.5 mmol) in ethanol (20 ml) NaBH_4 (0.5 g, 12 mmol) was added in small portions and the stirring continued for 12 h. The excess NaBH_4 was decomposed with water and

most of the ethanol was removed. The residue was taken up in chloroform, washed with water and brine, and dried. The solvent was removed and the residual solid crystallized from ethanol-hexane to yield the hydroxy acid (11, a) (0.05 g, 78%) m.p. 115°; IR (nujol) $\nu_{\max}$ 3280, 1720 cm^{-1} ; ^1H NMR ($\text{CDCl}_3 + \text{CF}_3\text{CO}_2\text{H}$) δ 0.87 (s, 3H, CH_3), 1.25 [s, 9H, $\text{C}(\text{CH}_3)_3$], 1.4–2.2 (m, 9H, methylene and angular), 2.57 (bt, $J = 8$ Hz, 1H, $\text{CH}\cdot\text{CO}_2\text{H}$) 3.59 [bt, $J = 10$ Hz, 1H, $\text{CH}\cdot\text{OC}(\text{CH}_3)_3$], 4.03 (dt, $J = 10$ and 8 Hz, 1H, CHOH), MS, m/e (relative intensity) 214 (36, $M-56$) 196 (43), 178 (40%); Found: C 66.28, H 9.66; $\text{C}_{15}\text{H}_{26}\text{O}_4$ requires C 66.63, H 9.69%.

4.6 ($\pm$)-Methyl 1 β -t-butoxy-5,6,7,7a-tetrahydro-7a β -methyl-5-keto-4-indancarboxylate, (2, a)

A solution of diazomethane in ether (76 ml, 0.076 mmol/ml) was added dropwise with stirring to a suspension of the unsaturated β -ketoacid (2, c) (1, 34 g, 5 mmol) in ether (50 ml). After stirring for 10 min, the solvent was removed and the residue crystallized from hexane to obtain the ester (2, a) (1.4 g > 99%); m.p. 76–77° (reported 76.5–77°); IR (nujol) $\nu_{\max}$ 1670, 1730 cm^{-1} ; ^1H NMR (CCl_4), δ 1.1 [s, 12H, CH_3 and $(\text{CCH}_3)_3$], 1.6–2.72 (m, 8H, methylene), 3.6 (bt, $J = 7$ Hz, 1H, $\text{CH}\cdot\text{O}$), 3.7 (s, 3H, CO_2CH_3).

4.7 ($\pm$)-Methyl 1 β -t-butoxy-7a β -methyl-3 $\alpha\alpha$, 4 β , 5,6,7,7a-hexahydro-5 β -hydroxy-4 α -indancarboxylate, (11b)

To a cooled and stirred solution of the ketoester (2, a) (0.7 g, 2.5 mmol) in ethanol (10 ml) NaBH_4 (0.23 g, 6 mmol) was added in small portions and the stirring continued for 12 h. After the usual work-up, the *trans* hydroxy ester (11, b) (0.65 g, 91%) was isolated; IR (CHCl_3) $\nu_{\max}$ 3600, 1735 cm^{-1} ; ^1H NMR (CCl_4) δ 0.8 (s, 3H, CH_3), 1.16 [s, 9H, $\text{C}(\text{CH}_3)_3$], 1.22–2.52 (m, 10H, methylene, angular and $\text{CH}\cdot\text{CO}_2\text{CH}_3$), 3.04 (bs, 1H, D_2O exchangeable, CHOH), 3.34 [t, $J = 8$ Hz, 1H, $\text{CH}\cdot\text{OC}(\text{CH}_3)_3$], 3.6 (s, 3H, CO_2CH_3), 3.62 (m, 1H, CHOH). Found: C 67.31, H 9.86; $\text{C}_{16}\text{H}_{28}\text{O}_4$ requires C 67.57, H 9.93%.

4.8 ($\pm$)-1 β -t-Butoxy-2,6,7,7a-tetrahydro-4-hydroxymethyl-7a β -methylindene, (12)

(a) A solution of the ketoacid (2, c) (2 g, 7.5 mmol) in dry THF (15 ml) was added dropwise to a stirred suspension of LiAlH_4 (0.5 g, 13 mmol) in dry ether (10 ml) at 0°, and the stirring continued for 1 h. The mixture was stirred for 4 h more at the room temperature. The excess LiAlH_4 was decomposed by the addition of water at 0°, followed by the addition of ice-cold 6N HCl (10 ml) and stirring for 1 h. The ethereal layer was separated, washed with water, aq. NaHCO_3 and brine, and dried. Removal of the solvent and purification of the residue by column chromatography (silica gel, CHCl_3) yielded the diene alcohol (12) (1.32 g, 75%); IR (neat) $\nu_{\max}$ 3450, 1640 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.9 (s, 3H, CH_3), 1.18 [s, 9H, $\text{C}(\text{CH}_3)_3$], 1.4–2.56 (m, 6H, methylene), 3.78 [t, $J = 7$ Hz, 1H, $\text{CH}\cdot\text{O}\cdot\text{C}(\text{CH}_3)_3$], 4.24, (s, 2H, CH_2OH); 5.49 (bt, 1H, vinylic), 5.8 (bt, 1H, vinylic); ^{13}C NMR (CDCl_3) δ 15.36 (q, CCH_3), 23.17 (t, CCH_2CCH_3), 28.57 [q, $\text{C}(\text{CH}_3)_3$], 33.64 (t, CCH_2 ; CH_2CCH_3), 38.13 (t, $\text{CCH}_2\text{CH}\cdot\text{O}$), 44.96 (s, CCH_3), 62.98 (t, CCH_2OH), 72.45 [s, $\text{C}(\text{CH}_3)_3$], 81.13 (d, $\text{CH}\cdot\text{O}$), 117.24 (d, vinylic CH), 125.7

(*d*, vinylic $\underline{\text{C}}\text{H}$), 132.99 (*s*, $\text{H}_3\text{C}-\underline{\text{C}}=\text{CH}$), 143.98 (*s*, $\text{HOCH}_2-\underline{\text{C}}=\text{CH}$); Found: C 76.35, H 10.18; $\text{C}_{15}\text{H}_{24}\text{O}_2$ requires C 76.22, H 10.24%.

(b) To a stirred and cooled (0°) suspension of LiAlH_4 (0.5 g, 13 mmol) in dry ether (10 ml) was added a solution of the ketoester (2, a) (2.1 g, 7.5 mmol) in dry ether (15 ml) and the stirring continued at 0° for 1 h and at the room temperature for 4 h. After the usual work-up, the diene alcohol (12) (1.5 g, 85%) was obtained.

(c) To a stirred and cooled (0°) suspension of LiAlH_4 (0.09 g, 23.6 mmol) in dry ether (100 ml) under N_2 was added a suspension of powdered, freshly sublimed AlCl_3 (1.17 g, 8.8 mmol) in ether (10 ml) and the mixture stirred for 1 h. A solution of the ketoester (2, a), (2.2 g, 7.9 mmol) in dry ether (100 ml) was added over a period of 20 min, the mixture stirred at 0° for 1 h and then at the room temperature for 30 min. The cooled (0°) mixture was treated with cold 6N HCl and stirred for 1 h. The product was extracted with ether, washed with brine and dried. Removal of the solvent afforded the diene alcohol (12) (1.76 g, 95%).

4.9 ($\pm$)-1 β -*t*-Butoxy-2,6,7,7a-tetrahydro-4-formyl-7a β -methylindene, (1, b)

(a) To a solution of the alcohol (12) (3.5 g, 14.8 mmol) in *n*-hexane (250 ml) was added active MnO_2 (35 g) and the mixture stirred. The progress of the oxidation was monitored by TLC. When all the alcohol had been consumed (6 h), the mixture was stirred for 5 min after dilution with ether. The crude material, after concentrating the solution, was chromatographed over neutral alumina ($\text{C}_6\text{H}_{14}-\text{CHCl}_3$) to afford the aldehyde (1, b) (2.8 g, 81%); IR (CHCl_3) ν_{max} 2750, 1690, 1650, 1610 cm^{-1} ; UV ($\text{C}_2\text{H}_5\text{OH}$) λ_{max} 222 nm (ϵ 16, 200); ^1H NMR (CDCl_3) δ 0.88 (*s*, 3H, $\underline{\text{CH}}_3$), 1.17 [*s*, 9H, $\text{C}(\underline{\text{CH}}_3)_3$], 1.52–2.47 (*m*, 6H, methylene), 3.79 [*t*, $J = 7$ Hz, 1H, $\underline{\text{CHOC}}(\text{CH}_3)_3$], 6.4 (*br*, 1H, vinylic), 6.69 (*br*, 1H, vinylic), 9.52 (*s*, $\underline{\text{CHO}}$); Found: C 77.07, H 9.48; $\text{C}_{15}\text{H}_{22}\text{O}_2$ requires C 76.88, H 9.46%.

(b) To a stirred and cooled (-78°) solution of oxalyl chloride (3.75 ml, 41 mmol) in dry CH_2Cl_2 (95 ml) was added DMSO (6.38 ml, 82 mmol) and after stirring for 20 min the alcohol (12) (3.5 g, 14.8 mmol) in CH_2Cl_2 (40 ml) was added dropwise. After another 20 min, triethylamine (26 ml, 185 mmol) was added and the mixture warmed to the room temperature, and 10 min later, poured into water. The aqueous layer was extracted thrice with CH_2Cl_2 and the combined CH_2Cl_2 layer was washed once with 1% HCl and then with 5% Na_2CO_3 , dried, concentrated and chromatographed [neutral alumina, $\text{C}_6\text{H}_{14}-\text{CHCl}_3$ (2:1)] to give the aldehyde (1, b) (3 g, 85%).

4.10 ($\pm$)-2,6,7,7a-Tetrahydro-1 β -hydroxy-4-formyl-7a β -methylindene, (1, a)

The diene aldehyde (1, b) (0.34 g, 1.5 mmol) was suspended in conc. HCl (6 ml) and stirred for 24 h under N_2 at 20° , followed by extraction with ether. The extract was washed with water and brine and then dried. Removal of the ether and purification of the residue by PTLC ($\text{C}_6\text{H}_{14}-\text{CHCl}_3$, 3:1) gave the hydroxy aldehyde (1, a) (0.22 g, 85%), identical with the one prepared by us earlier.

4.11 (+)-Methyl (1*S*, 7*aS*)-1-*t*-butoxy-5,6,7,7a-tetrahydro-7a-methyl-5-keto-4-indancarboxylate, (2, a)

Esterification of the carboxylic acid [(+)-2, c], prepared by the method of Micheli

et al (1975) and the starting material [(+)-10] for which was prepared by a recent method of Hajos and Parrish (1985), with diazomethane gave [(+)-2, a] in 99% yield; $[\alpha]_D^{25} + 30^\circ$ (CHCl_3 , C 1.0).

4.12 (+)-(1*S*, 7*aS*)-1-*t*-Butoxy-2,6,7,7*a*-tetrahydro-4-hydroxymethyl-7*a*-methylin-dene, (12)

Reduction of the ketoester [(+)-2, a] with aluminium hydride followed by the usual work-up gave the diene alcohol [(+)-12] in 96% yield; $[\alpha]_D^{25} + 59.2^\circ$ (CHCl_3 , C 1.0).

4.13 (+)-(1*S*, 7*aS*)-1-*t*-Butoxy-2,6,7,7*a*-tetrahydro-4-formyl-7*a*-methylin-dene, (1, b)

The chiral hydroxy compound [(+)-12] was oxidized by active MnO_2 or $\text{DMSO}-(\text{COCl})_2$ (Swern oxidation) to furnish the diene aldehyde [(+)-1, b] in > 80% yield; $[\alpha]_D^{25} + 40.6^\circ$ (CHCl_3 , C 1.0).

4.14 (+)-(1*S*, 7*aS*)-2,6,7,7*a*-tetrahydro-1-hydroxy-4-formyl-7*a*-methylin-dene, (1, a)

Removal of the *t*-butoxy group from the ether [(+)-1, b] by treatment with conc. HCl afforded the hydroxy aldehyde [(+)-1, a] in 85% yield, $[\alpha]_D^{25} + 36^\circ$ (CHCl_3 , C 1.0).

4.15 4-Methoxybut-1-yne, (18)

The title compound (18) was prepared by a modification of the method reported earlier (McCusker and Kraeger 1937). Acetylene was bubbled through a stirred suspension of sodamide, prepared from Na (9 g, 0.39 gatom) and dry ammonia (550 ml). To the resulting slurry of sodium acetylide was added dropwise 2-methoxyethyl bromide (48 g, 0.35 mmol) in 2 h, the bubbling of acetylene and stirring being continued throughout. The ammonia was allowed to evaporate and a saturated solution of NH_4Cl was carefully added. The mixture was cooled in a bath of ice-salt mixture and neutralized with 6*N* HCl . The product was distilled by heating the reaction mixture on a water-bath, then dried and redistilled to afford 4-methoxybut-1-yne (18) (20 g, 66%); b.p. $74-76^\circ$; IR (neat) ν_{max} 3300, 2850, 2150 cm^{-1} ; ^1H NMR (CCl_4) δ 1.9 (*t*, $J = 2\text{ Hz}$, 1H, $\text{C} \equiv \text{CH}$), 2.4 (*dt*, $J = 2$ and 7 Hz , 2H, $\text{CH}_2\text{C} \equiv \text{C}$), 3.35 (*s*, 3H, OCH_3), 3.45 (*t*, $J = 7\text{ Hz}$, 2H, OCH_2).

4.16 *N*-Diethylamino-5-methoxypent-2-yne, (19)

A mixture of 4-methoxybut-1-yne (18) (40 g, 0.48 mol), diethylamine (37 g, 0.5 mol), acetic acid (30 g, 0.5 mol), formalin (60 ml, 35%, 0.7 mol), CuCl (0.8 g, 0.008 mol) and water (40 ml) was stirred under N_2 for 60 h and then basified (pH 13) with aq. NaOH , saturated with $(\text{NH}_4)_2\text{SO}_4$ and extracted thrice with ethyl acetate. The extract was washed with brine and dried, and the solvent removed. The Mannich base (19) (50 g, 63%) was isolated by distillation; b.p. $135-140^\circ/60\text{ mm}$; ^1H NMR (CCl_4) δ 1.02 [*t*, $J = 7\text{ Hz}$, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$], 2.4 [*m*, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$ and $\text{CH}_2(\text{CH}_2\text{OCH}_3)_2$], 3.3 (*s*, 5H, OCH_3 and $\text{C} \equiv \text{CH}_2\text{N}$), 3.35 (*m*, 2H, CH_2O); Found: C 71.23, H 11.4, N 8.31; $\text{C}_{10}\text{H}_{19}\text{NO}$ requires C 70.96, H 11.32, N 8.28%.

4.17a *N*-Diethylamino-5-methoxypentan-3-one, (6)

(i) A mixture of the Mannich base (19) (3.3 g, 19.5 mmol), conc. H_2SO_4 (1.4 ml) and HgSO_4 (0.25 g, 0.8 mmol) in water (15 ml) was stirred under N_2 for 12 h at room temperature, then basified (pH 13) with aq. NaOH , saturated with $(\text{NH}_4)_2\text{SO}_4$ and extracted with ethyl acetate. The extract was washed with brine and the solvent removed. The residue was chromatographed over neutral alumina. Elution with C_6H_6 – CH_2Cl_2 (10:1) gave the starting compound (19) (1.02 g, 30%) and a subsequent elution with C_6H_{14} – CH_2Cl_2 (1:1) afforded the amino ketone (6) (0.44 g, 12%) as a liquid; IR (neat) ν_{max} 1705 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.02 (t, 3H, CH_3), 1.25 (t, 3H, CH_3), 1.52 (m, 10H, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$ and CH_2OCH_3), 3.28 (s, 3H, OCH_3), 3.64 (t, $J = 7$ Hz, 2H, OCH_2); MS, m/z (relative intensity) 187 (27, M^+), 86 [100%, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$]. Further elution with ethyl acetate gave polymeric material.

(ii) The aforementioned mixture of the Mannich base (19), conc. H_2SO_4 , HgSO_4 and water was stirred under N_2 at room temperature for 18 h. After the usual work-up and purification, (0.93 g, 25%) of the amino ketone (6) was obtained.

4.17b *1*-Chloro-5-methoxypentan-3-one (20): This compound, required for the preparation of the amino ketone (6) in an improved yield by the second method, was prepared by the following two procedures.

(i) To the powdered freshly sublimed AlCl_3 (67 g, 0.56 mol) in CH_2Cl_2 (250 ml) at 0° was added dropwise 3-methoxypropionyl chloride (56 g, 0.46 mol) and ethylene was bubbled through the mixture for 4–5 h, the temperature being maintained between 0 – 5° . The reaction mixture was poured into crushed ice containing conc. HCl (100 ml) and extracted with CH_2Cl_2 . The organic layer was washed successively with water, aq. NaHCO_3 , water and brine, and dried. After removal of the solvent under diminished pressure, the residue was chromatographed over neutral alumina. The first fraction (C_6H_{14} – C_6H_6 , 1:1) gave di-2-chloroethyl ketone (5.66 g, 8%), identified by its spectral analysis and comparison with an authentic sample (Baddeley *et al* 1953); IR (neat) ν_{max} 1715 cm^{-1} ; ^1H NMR (CCl_4) δ 2.92 (t, $J = 7$ Hz, 2H, CH_2CO), 3.74 (t, $J = 7$ Hz, 2H, CH_2Cl). The second fraction (C_6H_{14} – CHCl_3 , 1:3) yielded, after removal of the solvent, the unstable 1-chloro-5-methoxypentan-3-one (20) (34.8 g, 68%); b.p. 131–135°/5 mm; IR (neat) ν_{max} 1720 cm^{-1} ; ^1H NMR (CCl_4) δ 2.66 (t, $J = 7$ Hz, 2H, $\text{COCH}_2\text{CH}_2\text{O}$), 2.93 (t, $J = 6$ Hz, 2H, $\text{COCH}_2\text{CH}_2\text{Cl}$), 3.33 (s, 3H, OCH_3), 3.58–3.8 (m, 4H, CH_2O and CH_2Cl).

(ii) To a cooled and vigorously stirred solution of 3-chloropropionic acid (1.08 g, 10 mmol) in dry ether (40 ml) was added dropwise in 30 min an ethereal solution prepared from 2-methoxyethyl bromide (2.78 g, 20 mmol) and Li (0.3 g, 0.01 atom), under N_2 and the faintly turbid solution was stirred at room temperature for 4 h. To this was added dropwise under stirring ice-cold dil. HCl . The ethereal layer was separated and the aqueous phase was extracted thrice with ether. The combined extract was washed with aq. Na_2CO_3 and water, and dried. Removal of the solvent gave the chloromethoxy ketone (20) (0.35 g, 23%).

To a stirred ice-cold solution of diethylamine (1.46 g, 20 mmol) in benzene (15 ml) was added dropwise the chloromethoxy ketone (20) (1.5 g, 10 mmol) and

the mixture left for 4 h at 0°. It was basified (pH > 13) with dil. NaOH and extracted with ethyl acetate. After removal of the solvent and purification of the residue by chromatography the amino ketone (6) (1.5 g, 81%) was obtained.

4.18 (±)-5,6,7,7a-Tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione (3) and (±)-2,6-diketo-3-methyltricyclo(5,2,1,0)decan-8-ol, (4).

(a) A mixture of the aminoketone (6) (1.25 g, 6.5 mmol), the dione (5) (0.85 g, 7.6 mmol), pyridine (1.75 g, 22 mmol) and xylene (10 ml) was heated under reflux for 20 h. The mixture was diluted with CHCl_3 and washed successively with dil. HCl, water, aq. NaHCO_3 , water and brine. After removal of the CHCl_3 , PTS (1.25 g, 7 mmol) was added and the mixture was heated under reflux with a Decan-Stark attachment for 4 h, cooled, thoroughly washed with water, concentrated under vacuum and chromatographed over silica gel. Elution with CHCl_3 initially gave 5,6,7,7a-tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione(3) (0.71 g, 59%) which was further purified by short-path distillation, bath temp. 136–140° (2 mm); UV ($\text{C}_2\text{H}_5\text{-OH}$) λ_{max} 290 (ϵ 9,300), 300 nm (ϵ 11,000); IR (neat) ν_{max} 1710, 1670 cm^{-1} ; ^1H NMR (CCl_4) 1.28 (s, 3H, CH_3), 1.88 (s, 3H, olefinic CH_3) 1.6–2.82 (m, 4H, methylene), 6.32 (d, J = 3 Hz, 1H, olefinic α -H), 7.06 (d, J = 3 Hz, 1H, olefinic β -H); MS m/e (relative intensity) 176 (10, M^+), 161 (8), 133 (100%); Found: C 74.91, H 6.9; $\text{C}_{11}\text{H}_{12}\text{O}_2$ requires C 74.97, H 6.86%.

Subsequent elution with CHCl_3 furnished the white crystalline compound (4) (0.12 g, 12%), which was recrystallized from $\text{C}_6\text{H}_{14}\text{-C}_6\text{H}_6$; m.p. 170–171° (reported 172–174°), IR (nujol) ν_{max} 3360, 1735, 1690 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.13 (s, 3H, CH_3), 1.62–2.66 (m, 10H, methylene and methine protons), 4.9 (s, 1H, OH exchangeable with D_2O); MS m/e (relative intensity) 194 (30, M^+). 69 (100%).

(b) A mixture of the amino ketone (6) (0.6 g, 3.1 mmol), the dione (5) (0.42 g, 3.8 mmol), PTS (0.85 g, 11 mmol) and xylene (50 ml) was heated under reflux for 20 h. After the usual work-up and purification the dienedione (3) (0.3 g, 49%) and the tricyclic keto alcohol (4) (0.017 g, 14%) were obtained.

4.19 Catalytic hydrogenation of (±)-5,6,7,7a-tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione (3)

An ethanolic solution of dienedione (3) (0.26 g, 1.5 mmol) was hydrogenated over 5% Pd-C catalyst (0.03 g) for 4 h, when a little more than 1 equivalent of H_2 was absorbed. The catalyst was filtered off and the ethanol removed under vacuum and the residue chromatographed over silica gel. ($\text{C}_6\text{H}_{14}\text{-CH}_3\text{CO}_2$, C_2H_5 , 1:1) to give the known monoenone (9,d) (0.25 g, > 99%). The structure was confirmed by a direct comparison of the spectral data and TLC with those of an authentic specimen.

4.20a (±)-2-(5'-Methoxy-3'-ketopentyl)-2-methylcyclopentan-1,3-dione (23): A solution of the amino ketone (6) (1.9 g, 10 mmol) and the dione (5) (1.1 g, 10 mmol) in dry C_6H_6 and pyridine (2.3 g, 30 mmol) was stirred at room temperature for 24 h and then cooled, diluted with C_6H_6 , washed successively with dil. HCl, water, aq. NaHCO_3 and water, and dried. The solvent was removed under vacuum and the residue on short-path distillation gave the cyclopentandione (23) (1.54 g, 66%); bath temp. 176–183° (1 mm); IR (neat) ν_{max} 1750, 1710, 1705,

1110 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.11 (s, 3H, CH_3), 1.92 (t, $J = 7$ Hz, 2 $\text{CH}_2\text{-CH}_3$), 2.5 (t, $J = 7$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)$), 2.63 (t, $J = 6$ Hz, 2H, OCH_2), 2.81 (s, 2H, ring methylene), 2.83 (s, 2H, ring methylene), 3.32 (s, 3 OCH_3), 3.62 (t, $J = 6$ Hz, 2H, OCH_2); ^{13}C NMR (CDCl_3) δ 18.66 (q, CH_3), 27.77 (t, $\text{CH}_2\text{C}(\text{CH}_3)$), 34.73 (t, ring methylene), 37.07 (t, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)$), 42.1 (t, OCH_2CH_2), 55.08 (s, $\text{C}(\text{CH}_3)$), 58.66 (q, OCH_3), 67.3 (t, OCH_2), 208.16 (acyclic C=O), 215.77 (s, ring C=O); MS, m/e (relative intensity) 226 (10, M^+), 2 (20), 125 $^+$ (100%); Found: C 63.58, H 8.04; $\text{C}_{12}\text{H}_{18}\text{O}_4$ requires C 63.7, H 8.02%.

4.20b ($\pm$)-2-(3'-ketopent-4'-enyl)-2-methyleyclopentan-1,3-dione (21): (i) A solution of di-2-chloroethyl ketone (5 g, 33 mmol) in monoglyme (20 ml) was added with stirring at room temperature under N_2 to a suspension of the sodium salt of the dione (5), prepared from Na dust (0.9 g, 0.4 g atom) and the dione (5) (4.45 g, 40 mmol) in monoglyme (10 ml) at 0–5 $^\circ$. The mixture was stirred for 12 h at room temperature and then cooled, acidified with dil. HCl, saturated with NaCl and extracted with ether. The extract was washed with aq. NaHCO_3 and water, and dried. Removal of the solvent gave the vinyl triketone (21) (8.5 g, 70%), IR (neat) ν_{max} 1760, 1725, 1685, 1620 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.14 (s, 3H, CH_3), 1.95 (t, $J = 7$ Hz, 2H, $\text{CH}_2\text{C}(\text{CH}_3)$), 2.62 (t, $J = 7$ Hz, 2H, $\text{COCH}_2\text{-C}(\text{CH}_3)$), 2.7–2.94 (4H, ring methylene), 5.86 (dd, $J = 9$ and 2 Hz, 1H, vinylic), 6.16–6.29 (m, 2 vinylic).

(ii) *Base-catalysed addition to the vinyl triketone* (21) To a solution of sodium methoxide (0.5 g, 10 mmol) in methanol (10 ml) was added at 0 $^\circ$ in 10 min a solution of the vinyl triketone (21) in methanol (10 ml). The solution was then allowed to attain the room temperature and stirred for 5 h. The methanol was removed under vacuum and the residue, after acidification with 2% HCl, was extracted with ether. The extract was dried, the solvent removed and the residue chromatographed over silica gel ($\text{C}_6\text{H}_{14}\text{-CH}_3\text{CO}_2\text{C}_2\text{H}_5$, 2:1) to obtain the methoxy triketone (23) (3.1 g, 66%).

4.21 ($\pm$)-3a,4,5,6,7,7a-Hexahydro-3a-hydroxy-4-(1',3'-diketo-2'-methyleyclopentano-2'-methylene)-7a-methylindene-1,5-dione (8)

A mixture of the triketone (23) (0.57 g, 2 mmol), the dione (5) (0.28 g, 2.5 mmol), pyridine (0.6 g, 7.8 mmol) and dry benzene (10 ml) was stirred at room temperature for 12 h and then diluted with benzene and washed successively with dil. HCl, aq. NaHCO_3 and water, and dried. After removal of the solvent, the solid residue was crystallized to yield the hydroxy tetraketone (8) (0.61 g, 74%), mp 192–194 $^\circ$; IR (nujol) ν_{max} 3405, 1740, 1730, 1710 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$) δ 0.94 [s, 3H, $\text{COC}(\text{CH}_3)\text{CHOH}$], 1.06 [s, 3H, $\text{CO}(\text{CH}_3)\text{CO}$], 1.32–2.78 (m, 15 methylene and methine), 6.8, (s, 1H, OH, exchangeable with D_2O); ^{13}C NMR ($\text{DMSO}-d_6$) 11.84 [q, $\text{C}(\text{CH}_2)\text{COH}$], 20.68 [q, $\text{CO}(\text{CH}_3)\text{CO}$], 23.07 ($\text{CH}_2\text{-CH}_2\text{CCH}_3$), 25.72 (t, $\text{C}(\text{CH}_2)$), 29.92 (t, HOC), 32.64 (t, $\text{CH}_2\text{CH}_2\text{CCH}_3$), 34.54 (t, $\text{HOCCH}_2\text{CH}_2$), 36.15 (t, $\text{COCH}_2\text{CH}_2\text{CO}$), 36.69 (t, $\text{COCH}_2\text{CH}_2\text{CO}$), 48.26 (d, COCH), 52.12 (s, HOCCH_2CO), 53.54 (s, $\text{CO}(\text{CH}_3)\text{CO}$), 86.02 (CHO), 207 [s, $\text{COC}(\text{CH}_3)\text{CO}$], 217.78 (s, CH_3COCH), 218.1 ($\text{COC}(\text{CH}_3)\text{OCH}$); MS m/e (relative intensity) 306 (27, M^+), 288 (12), 260 (8), 177 (25), 125 (85), 113 (100%); Found: C 66.7, H 7.21; $\text{C}_{17}\text{H}_{23}\text{O}_6$ requires C 66.65, H 7.24%.

Acknowledgements

This paper is based on part of the Ph.D. thesis of one of the authors (RSB) submitted to the Indian Institute of Science, Bangalore. One of the authors (RSB) acknowledges the financial support of the Department of Atomic Energy.

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Rapid chemical synthesis of d(CACGTG) in milligram amounts by solution-phase phosphotriester chemistry

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MS received 24 August 1987; revised 14 December 1987

Abstract. This paper reports an optimised method for chemical synthesis of short oligodeoxyribonucleotides in milligram amounts by solution-phase phosphotriester chemistry. The procedure is a slight modification of one reported earlier in the literature. Detailed experimental procedures for condensation, deprotection and purification are described. The efficiency of the method is demonstrated by the synthesis of a hexamer, d(CACGTG), in good yields and high purity. The homogeneity of the product and the sequence composition are shown by 270 MHz ¹H NMR spectrum.

Keywords. Oligodeoxyribonucleotide synthesis; chemical synthesis of d(CACGTG); ¹H NMR of oligonucleotides.

1. Introduction

In spite of rapid developments in synthetic methodologies for oligodeoxynucleotides (Gait 1984; Sonveaux 1986) the preparation of sufficient quantities of these in the high purity required for X-ray and NMR studies is still a formidable challenge. The choice of synthetic strategy for scaling-up depends on the required length and the choice of purification protocols becomes crucial when one needs large amounts of oligonucleotides in high purity. We have previously analysed the suitability of various supports (Ganesh 1985; Minganti *et al* 1985) for solid-phase synthesis of longer (~ 23-mer) oligodeoxynucleotides in milligram amounts. In this paper, we report an optimised procedure for solution-phase phosphotriester synthesis of d(CACGTG)** in milligram amounts. The method is of general application for synthesis of short oligodeoxynucleotides (6-8-mers).

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**Structure of DNA fragments is represented only by the base sequence, e.g., in d(CACGTG), d stands for deoxy.

2. Chemical synthesis

2.1 Choice of synthetic method

In the past, a lot of effort has been directed towards synthesis of oligodeoxynucleotides by solid-phase synthesis and by different chemical approaches. These methods result in smaller quantities of less pure products than does synthesis in solution but meet most of the present needs of molecular biologists. The solid-phase method works best for smaller amounts (from micrograms up to a milligram); the scaling-up to prepare larger amounts (milligrams) introduces considerable problems. (Gait 1984; Minganti *et al.* 1985). However, little effort has been concentrated till now on improving the solution phase synthesis. Solution phase synthesis appears to be the best method for obtaining large amounts of short oligomers required for spectroscopic, structural and physicochemical studies. The ultimate purity of the product is high because of successive purifications after each step of condensation. The phosphotriester chemistry is the only method available at present for solution-phase synthesis and our present approach is therefore dependent on the use of this methodology.

2.2 The synthetic cycle

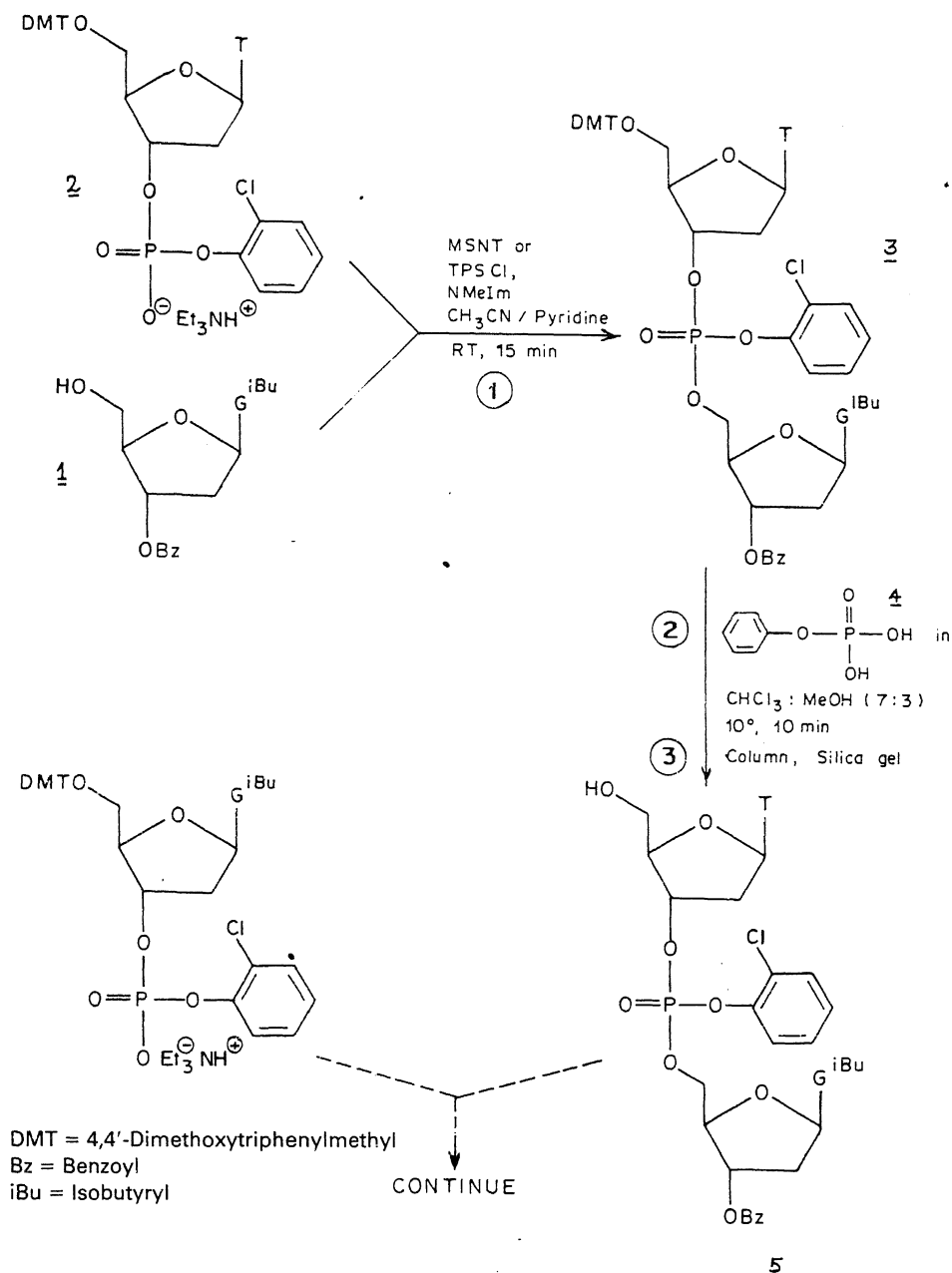
Our present phosphotriester method is an optimised extension of that reported by Chaudhari *et al.* (1984). Here (scheme 1) the DNA chain is extended in the 3' → 5' direction as in normal solid-phase synthesis. Each synthetic cycle consists of three consecutive steps: (1) condensation, (2) deprotection and (3) purification. During the first step (scheme 1) a 3'-terminal block such as **1** is condensed with a 3'-(2-chlorophenyl) phosphate ester of an N-protected 2' deoxyribonucleotide **2**. The condensing agent used is either 1-(mesitylene-2 sulphonyl) 5-imidazo [1,2-*b*] triazole (MSNT) or triisopropyl benzenesulphonyl chloride (TPSCl) in combination with a nucleophilic catalyst such as 1-methylimidazole (Himov *et al.* 1982). The reaction solvent used is acetonitrile for the first 3 cycles, and pyridine for further cycles. The progress of the reaction is monitored by thin layer chromatography over silica gel.

The 5',3'-O-protected dinucleotide (**3**) product of the first step is then deprotected at the 5'-position in the second step. This is achieved by treatment of the dinucleotide **3** with a solution of phenyl dihydrogen phosphate in chloroform-ethanol. A deep orange-red colour is produced instantaneously due to the liberated dimethoxytrityl cation. After work-up, the product **5** is taken to the third step of the cycle for rapid purification over silica gel.

The column was eluted first with chloroform (1-2 bed volumes) to remove non-nucleotidic impurities such as dimethoxytritanol liberated during the deprotection. The desired product **5** is then eluted with anhydrous tetrahydrofuran-pyridine (3:1) and recovered from the eluant. After drying, this product is used as the 5'-hydroxyl component for initiating the next cycle (scheme 1).

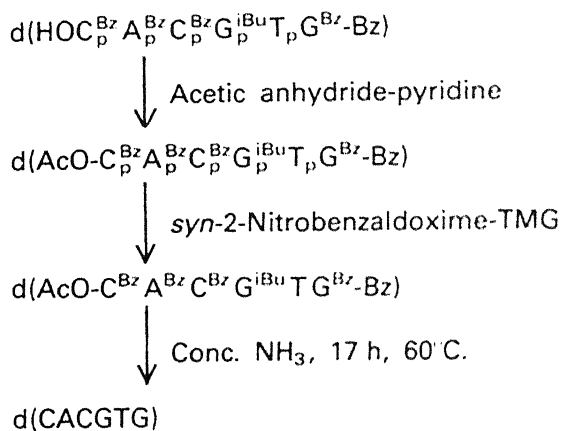
2.3 Deprotection and purification

At the end of the complete synthesis, the product oligomer obtained carries a terminal 5'-hydroxyl group (scheme 2). This is acetylated with acetic anhydride-



Scheme 1

pyridine and then subjected to a two-stage deprotection procedure. First, it is treated with *syn*-2-nitro benzaldoximate reagent to remove the 2-chlorophenyl phosphate protection and this is followed by treatment with concentrated ammonia to effect all N- and O-deprotections. The totally unblocked product is passed through a Sephadex G-15 gel filtration column to remove small molecule impurities. The product which elutes out in the void volume is then purified by fast



d = Deoxy

Ac = Acetyl

A^{Bz} = 6-N-Benzoyl-2'-deoxyadenosine

C^{Bz} = 4-N-Benzoyl-2'-deoxycytidine

G^{iBu} = 2-N-Isobutyryl-2'-deoxyguanosine

p = Phosphate groups protected by 2-chlorophenyl

Scheme 2

protein liquid chromatography (FPLC) on an anion-exchange Mono Q column using a linear gradient from 0.1 M aqueous sodium hydroxide to 0.1 M aqueous sodium hydroxide containing 0.8 M sodium chloride. Figure 1 illustrates an analytical FPLC chromatogram of the crude product. The major peak from a preparative run was collected, neutralised to pH 7, and then desalted over a Sephadex G-15 column.

Using this procedure, we have synthesised oligomers (6–8-mers) in high purity and in milligram amounts. The isolated yields varied in the range of 70–85% per synthetic cycle leading to a 25–30% overall yield before FPLC purification.

3. Discussion

The modifications used in our procedure for solution-phase synthesis are based on previous experience (Effimov *et al* 1982; Rajendrakumar *et al* 1985) with solid-phase synthesis. The 3'-terminal nucleotide **1** used here carries an acetyl or benzoyl group at the 3' position whereas in the solid-phase synthesis it is attached to the polymer matrix. The phosphate component **2** added during every cycle is identical to the phosphotriester monomers of solid-phase synthesis. The solvent used for the condensation during the first three steps was acetonitrile since reactions are faster in this solvent compared to pyridine (Effimov *et al* 1982). However, after the trinucleotide stage, because of the low solubility of the 5'-hydroxyl component in acetonitrile, the solvent used was pyridine. The condensing agent used was either MSNT or TPSCI in combination with a nucleophilic catalyst such as 1-methylimidazole.

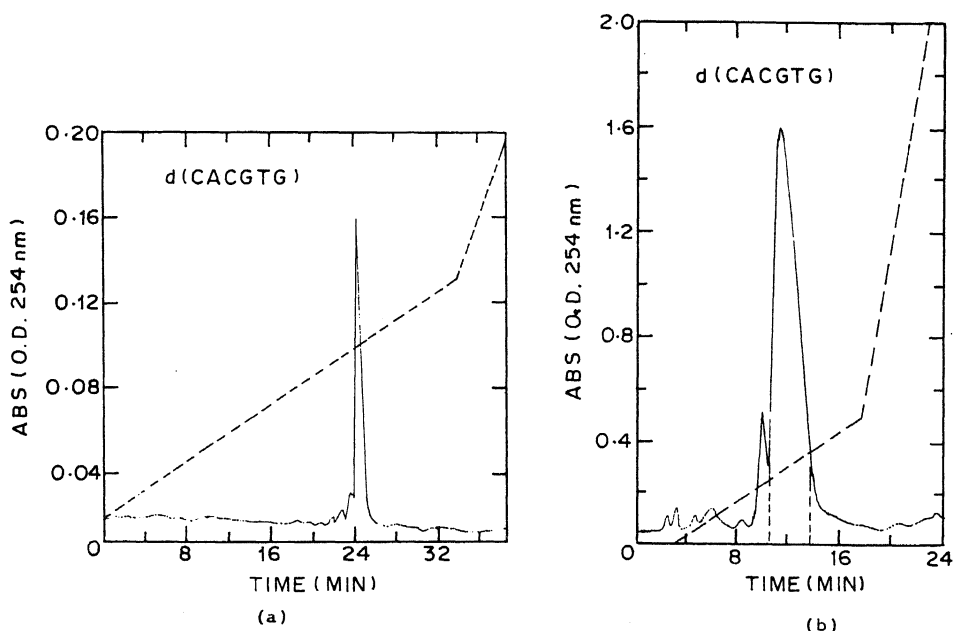


Figure 1. Analytical (a) and preparative (b) FPLC chromatograms. FPLC (Pharmacia) system consisted of two P 500 pumps, a GP 250 gradient programmer, a 5 MPa mixer, a V-7 sample injector and a DP-2 dual wavelength detector fixed at 254 nm. Column: Mono Q (Pharmacia) 5/5 (analytical) and 10/10 (preparative). Solvents: 0.1 M aq. NaOH pH 12 (low) and 0.1 M aq. NaOH with 0.8 M NaCl pH 12 (high). Flow rate: 0.5 ml/min (analytical) and 1.5 ml/min (preparative).

The reactions can be conveniently monitored by thin layer chromatography over silica gel. The phosphate monomers **2** added at every cycle have low r_f value ($\sim 0.04-0.05$) and show up as orange-red spots (trityl-positive) on t.l.c. after acid-spray. The 5'-hydroxy component **1** cannot be visualised in a similar way; however, when heated after the acid-spray it shows up as a dark spot. The phosphate component **2** is always taken in slight excess (1.2 equivalents) over the hydroxy component **1**. The completion of the condensation reaction is signalled by the total disappearance of **1** and appearance of a higher r_f trityl-positive spot due to **3**. Beyond the trinucleotide stage, the phosphate components are taken in 1.4-equivalent excess over the hydroxy component to drive the reaction to completion. It should be pointed out that for the eventual success of this method, the hydroxy component must disappear totally at every step; otherwise it is very difficult to separate it from the product since they have very close r_f values.

The 5'-deprotection of the product **3** is done with phenyl dihydrogen phosphate **4**. The reaction with this reagent in addition to being faster seems to cause less depurination as compared to either benzenesulphonic acid or dichloroacetic acid. The reaction can be assayed by t.l.c. as the trityl-positive product **3** is converted into a slightly slower moving trityl-negative product **5**. The liberated tritanol moves almost with the solvent front. The end product of the cycle (**5**) is purified by a rapid column chromatography over silica gel (Chaudhari *et al* 1982).

It can be seen from table 1 that the total time required for the first synthetic cycle is about 150 min. The four other cycles required for synthesis of a hexamer

Table 1. Time table for each cycle of coupling

		(Min)
Step 1	Reaction	15
	Work-up	15
Step 2	Reaction	10
	Work-up	10
Step 3	Column	60-80
Total		150 min cycle

were carried out in the same way. After the five cycles had been completed, material obtained after the final column chromatography was acetylated with acetic anhydride-pyridine before subjecting it to deprotection steps as in solid phase synthesis. After the ammonia treatment, the product was passed over a filtration column (Sephadex G-15) to separate the oligonucleotide product from deprotecting agent and other small molecule impurities. The product (6-8 mg) elutes out in the void volume. The crude product thus obtained is almost always 90-95% pure as shown by analytical anion-exchange FPLC (figure 1). However for spectroscopic and crystallographic work, this material is further purified by preparative FPLC over anion-exchange FPLC column. The detailed purification strategies for preparative purification, particularly optimised for self-complementary sequences, are being reported elsewhere.

To substantiate the purity and authenticity of the product, we have shown here (figure 2) the 270 MHz ^1H NMR spectrum of the synthesised d(CACGTG). The aromatic proton signals from the six base residues, appearing in the region $\delta^+ 0-8$, clearly support the base composition. The presence of a single thymidine residue is indicated by a lone methyl signal at $\delta 1.45$ and a singlet due to H6 at $\delta^+ 0.5$. The presence of two cytidines is indicated by two doublets for H6 protons, one for each cytidine, at $\delta 7.2$ and $\delta 7.6$. The doublets for the corresponding H5 protons of the two cytidines occur at $\delta 5.92$ and $\delta 5.32$, the former overlapping with glycosidic H1' sugar protons.

The hexamer d(CACGTG), which is self-complementary, exists as a duplex under the spectrum-recording conditions, as evidenced by a good dispersion and general non-equivalence of signals seen in the ^1H NMR spectrum. Single-strand structures, being random coils, give averaged spectrum which is just an additive spectrum of four bases showing equivalence among bases of the same kind. The total assignments of all signals (sugar and base protons) in d(CACGTG) have been completed by two-dimensional NMR techniques, and from COSY and NOE experiments. These assignments conform to the symmetry of a duplex structure. These and other spectroscopic analyses (CD, ^{31}P NMR) which are reported elsewhere have shown that this sequence has a distorted B-DNA conformation. The sequence d(CACGTG) is homologous to part of the bacteriophage P22 DNA operator region which is involved in interaction with *mnt* repressor protein. The structural results reported here are therefore of considerable importance to study of mechanisms of DNA-protein interactions.

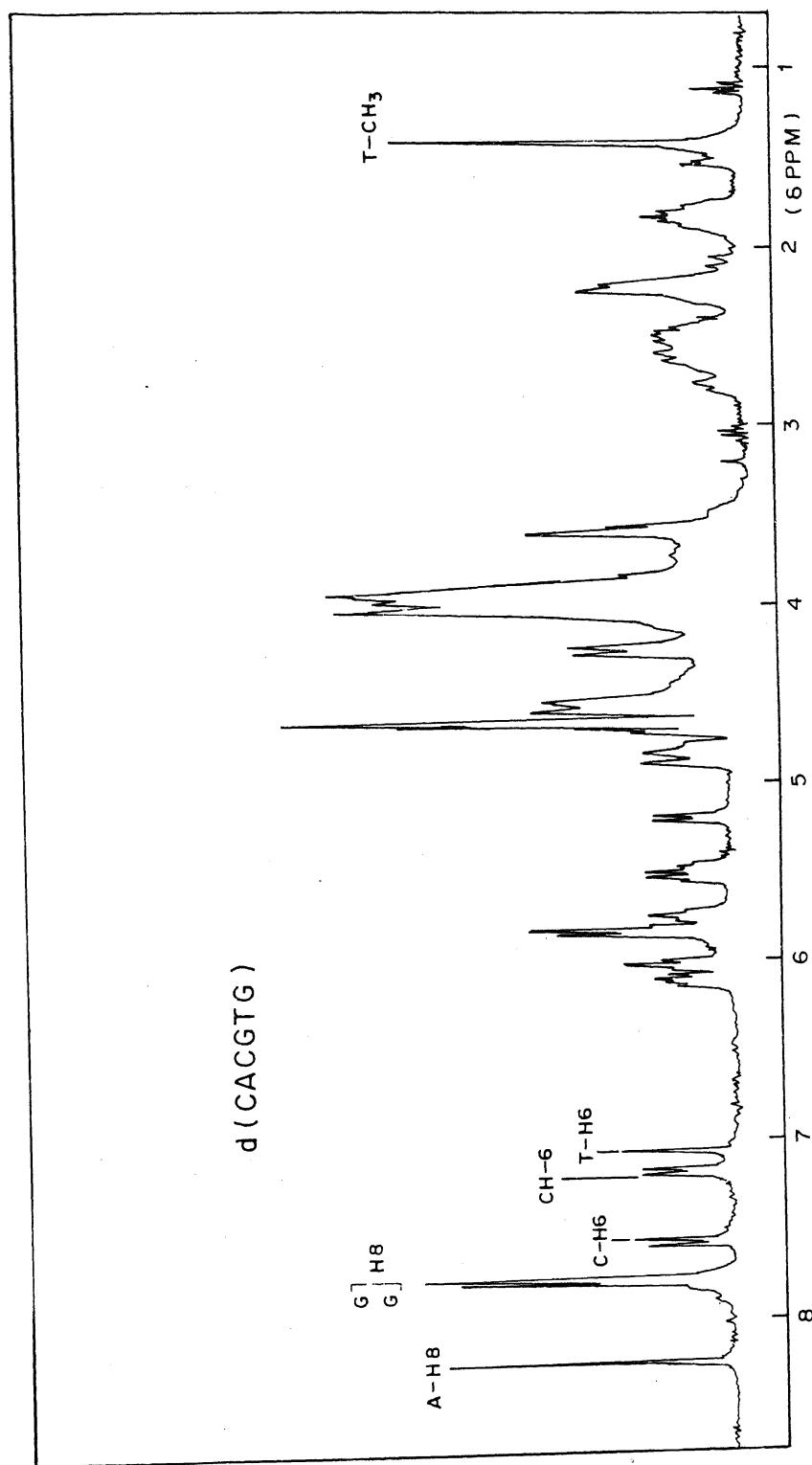


Figure 2. 270 MHz proton NMR spectrum of *d*(CACGTG) at 25°C. Sample concentration: 2 mg in 0.5 ml (~4 mm) of phosphate buffer (0.02 M), pH 7.5. Solution was lyophilized (3 times) and redissolved in 0.5 ml D₂O.

4. Experimental

The N,O-protected nucleotides and nucleosides were synthesised according to procedures reported previously (Rajendrakumar *et al* 1985). Methylimidazole and phenyl dichlorophosphate were procured from Fluka, Switzerland. Pyridine GR (E Merck, India) was refluxed and distilled over ninhydrin followed by distillation over calcium oxide. Acetonitrile and dichloromethane (E Merck, India) were distilled over phosphorus pentoxide before use. 2,4,6-Triisopropylbenzenesulphonyl chloride (Sigma, USA) was recrystallised from hexane. 1-(Mesitylene-2-sulphonyl)-3-nitro-1,2,4-triazole (MSNT) was prepared according to Gait *et al* (1984). All column chromatographic purifications were done over Merck Kieselgel 60 (Art. 9385) and monitored by t.l.c. over pre-coated fluorescent silica gel t.l.c. plates (Merck Art. 5554). The spots were visualised by UV lamp and by spraying with 60% perchloric acid-ethanol (3:2) for trityl derivatives. Compounds without the trityl group gave dark spots on spraying with the above reagent followed by heating. The 3'-terminal block 1 was prepared according to Denny *et al* (1982) and phenyl dihydrogen phosphate was synthesised by hydrolysis of phenyl dichlorophosphate (Owen *et al* 1974). The general protocol of the chemical synthesis is illustrated by the following procedure for the chemical synthesis of d(CACGTG).

Step (1): The phosphodiester block DMT-T-p (2, 140 mg, 0.18 mmole) and the 3'-terminal nucleoside (1, HO-dG-Bz, 72 mg, 0.15 mmole) were dried by coevaporation (2 times) and dissolved in with dry acetonitrile (1 ml/0.1 mmole of 1, 1.5 ml) under anhydrous conditions and treated with the condensing agent (0.45 mmole, TPSCI 140 mg or MSNT 133 mg) and 1-methylimidazole (0.9 mmole, 72 μ l). The reaction mixture was stirred at room temperature. The reaction, followed by t.l.c., was essentially complete within 10 min. Excess reagents were destroyed by treatment with aq. NaHCO_3 and the product was extracted into chloroform (3 $\times$ 20 ml). The chloroform layer was washed with water (10 ml) and the dried (Na_2SO_4) organic layer was concentrated under reduced pressure to yield a colourless foamy material of the protected dinucleotide 3. The total time to complete step 1 was 30 min. The product was taken to step 2 without any characterization.

Step (2): The material from step 1 was dissolved in chloroform-methanol (95:5, v/v, 6 ml), cooled at 10°C and treated with solid phenyl dihydrogen phosphate 4 (260 mg, 1.5 mmole). An instantaneous orange-red colour was produced. After 5–10 min (check t.l.c.) the reaction mixture was diluted with chloroform (20 ml) and washed with aq. NaHCO_3 . The dried organic layer on evaporation gave a foamy gum which was purified by step 3 to give 5.

Step (3): The material from step 2 was dissolved in chloroform (1.5 ml) and loaded uniformly over a short column (2 cm i.d.) of Merck silica gel (8 g). The column was washed with chloroform (~ 20 ml), when a pale yellow band separated and eluted out. This was then followed by elution with anhydrous tetrahydrofuran-pyridine (3:1, v/v, 40 ml) when the desired product, 5 was obtained in the eluant. This was recovered after evaporation under reduced pressure and repeatedly coevaporated with dichloromethane. The product 5 ($\text{T}_p\text{G}^{\text{Bz}}\text{-Bz}$, 120 mg, 90% yield) was dried over $\text{P}_2\text{O}_5\text{-KOH}$ in a vacuum desiccator and used for initiating the next cycle.

Table 2 Reaction conditions* for synthetic cycles.

3'-component (mg, mmole)	5'-component (mg, mmole)	Condensing agent (mg, mmole)	N-Methyl- imidazole (μ l, mmole)	Product (mg, yield)
d(I _p G ^{Bz} -Bz) (115, 0.13)	DMT-dG ^{Bz} _p (140, 0.15)	TPSCI (117, 0.39)	62; 0.78	d(G ^{Bz} _p T _p G ^{Bz} -Bz) (144, 80%)
d(G ^{Bz} _p I _p G ^{Bz} -Bz) (140, 0.11)	DMT-dC ^{Bz} _p (130, 0.14)	TPSCI (90, 0.3)	48; 0.6	d(C ^{Bz} _p G ^{Bz} _p T _p G ^{Bz} -Bz) (140, 70%)
d(C ^{Bz} _p G ^{Bz} _p I _p G ^{Bz} -Bz) (140, 0.08)	DMT-dA ^{Bz} _p (106, 0.11)	MSNT (71, 0.24)	38; 0.48	d(A ^{Bz} _p C ^{Bz} _p G ^{Bz} _p T _p G ^{Bz} -Bz) (126, 70%)
d(A ^{Bz} _p C ^{Bz} _p G ^{Bz} _p I _p G ^{Bz} -Bz) (120, 0.08)	DMT-dC ^{Bz} _p (72, 0.08)	MSNT (45, 0.15)	25; 0.3	d(C ^{Bz} _p A ^{Bz} _p C ^{Bz} _p G ^{Bz} _p T _p G ^{Bz} -Bz) (144, 70%)

The 3'-component, 5'-component, condensing agent and N-methylimidazole in the given amounts were dissolved in 1.5 ml of acetonitrile or pyridine and stirred at room temperature for 15 minutes before work-up.

Four more cycles were carried out similarly according to conditions shown in table 2. After the final cycle, the product obtained was subjected to the following sequence to yield the completely deblocked d(CACGTG).

d(AcO-C^{Bz}_pA^{Bz}_pC^{Bz}_pG^{Bz}_pT_pG^{Bz}-Bz):

d(C^{Bz}_pA^{Bz}_pC^{Bz}_pG^{Bz}_pT_pG^{Bz}-Bz) (140 mg) was treated with acetic anhydride (0.6 ml) and pyridine (1.5 ml) at room temperature for 2 h. The reaction mixture was poured into ice-water and stirred for 10 min. It was then extracted into chloroform (25 ml), washed with aq. NaHCO₃ and dried over Na₂SO₄. The organic layer on concentration gave a foamy acetate product (130 mg, 92%).

d(CACGTG): The acetate obtained above was dissolved in dioxane-water (1:1, v/v, 10 ml) and treated with *syn*-2-nitrobenzaloxime (400 mg) followed by tetramethylguanidine (0.27 ml). The reaction mixture was kept at room temperature for 14 h and then heated at 60°C for 3 h. It was lyophilized and then treated with concentrated ammonia (30 ml) in a sealed flask for 20 h at 60°C. The ammonia was evaporated and the product was passed through a Sephadex G-15 column (bed volume 120 ml) and eluted with 20% methanol-water. The eluted fractions were monitored by UV detector and the major peak eluting in the void volume was lyophilized. The residue was then purified over FPLC (for conditions see legend to figure 1) to obtain d(CACGTG) (70 mg, 30% overall yield).

5. Conclusions

In this paper, we have demonstrated an optimized protocol for a rapid, large-scale chemical synthesis of short oligodeoxynucleotides by solution-phase phosphotriester chemistry. In experienced hands, the protocol consumes only 150 min per cycle and can be conveniently scaled up to yield 6–8-mers in hundred-milligram

quantities. As indicated by ^1H NMR, the purity of the products after a preparative FPLC is extremely good and is acceptable for spectroscopic and crystallographic work.

Acknowledgements

The authors thank the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, for recording the NMR spectrum. GVRK gratefully acknowledges the award of a fellowship by the Council of Scientific and Industrial Research, New Delhi.

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Pulse radiolysis study of one-electron oxidation of thionine in aqueous solutions

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Abstract. One-electron oxidation of thionine has been studied using specific oxidizing radicals such as Cl_2^- , Ti(II) and N_3 generated by pulse radiolysis of aqueous solutions. The semioxidized thionine exhibited three pK 's indicating four conjugate acid-base forms. N_3 radicals were found to be less efficient in oxidizing thionine as compared to Cl_2^- , Ti^{2+} and Ti(OH)^+ . The rate constants for electron abstraction from thionine by Cl_2^- , Ti^{2+} , Ti(OH)^+ , Ti(OH)_2 and N_3 were evaluated. The spectra of different protonated forms of semioxidized thionine and the extinction coefficients at λ_{max} are presented. Reaction of OH radicals with thionine gave transient products whose spectra and acid-base properties were different from those of semioxidized thionine. The rate constant for formation of the product transient agrees well with competition kinetic value for reaction of OH with thionine reported earlier.

Keywords. Pulse radiolysis; one-electron oxidation; thionine oxidation.

1. Introduction

The one-electron reduction of thionine has been the subject of many investigations in the past, employing flash photolysis and pulse radiolysis techniques. Recently it has been shown (Guha *et al* 1987) that many organic radicals generated in pulse radiolysis experiments are able to bring about one-electron reduction of this molecule, and from a correlation of the efficiency of reduction of thionine and the standard potential for oxidation of the radical, the standard potential for the one-electron reduction of this compound was inferred. This value is in fairly good agreement with the indirect estimate made in the past (Rabinowitch 1940). There are no reports of one-electron oxidation of thionine in the literature. Kamat and Lichtin (1982), had however, attributed a transient absorption spectrum with a maximum at 480 nm observed in laser flash photolysis of thionine in aqueous solution (at pH $\sim$ 2) to the semioxidized form resulting from a net one electron transfer between the ground and excited triplet states of the molecule. There is, however, no direct proof to show that the species so observed is in fact the semioxidized form. We have therefore carried out pulse radiolysis experiments to find out whether one-electron oxidation of thionine can be directly observed via the use of well-known one-electron oxidants such as OH, Cl_2^- , Ti^{2+} , I_2^- , Br_2^- and N_3 that can be generated in aqueous solutions. The results of these investigations are reported

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here. Reaction of SO_4 with thionine could not be studied as there was precipitation on addition of $\text{K}_2\text{S}_2\text{O}_8$ to aqueous thionine solution.

2. Experimental

Thionine used in this study was from Fluka and was used after purification as described earlier (Guha *et al* 1982). Other chemicals were either BDH 'Analar' or E Merck 'GR' grade. 'IOLAR' grade N_2 , O_2 and N_2O from Indian oxygen were used for saturating the solutions. The pH of the solution was adjusted using H_2SO_4 , NaH_2PO_4 and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ and NaOH in the appropriate ranges. The pulse radiolysis experimental set up used in this study has been fully described earlier (Guha *et al* 1987). In all the experiments 25 nS electron pulses were employed and dosimetry was carried out using air saturated 0.05 mol dm^{-3} KCNS for which $G\varepsilon = 21,522 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ per 100 eV at 500 nm (Fielden 1982).

3. Results

Irradiation of water by ionizing radiations generates both oxidizing (OH) and reducing (e_{aq}^- , H) species. In oxygen saturated acid media ($\text{pH} < 4$) the reducing species are completely converted to HO_2 radicals within about $3 \mu\text{s}$ following a 25 nS pulsed electron irradiation. On pulsing solutions, which also contained 0.1 mol dm^{-3} *t*-butanol as scavenger for the OH radical and $5 \times 10^{-5} \text{ mol dm}^{-3}$ of thionine, no transient light absorbing species were observed, thus revealing the inertness of HO_2 towards thionine. However, when *t*-butanol was absent, a transient spectrum was observed (figure 1, curve a) which had maxima at 385, 475 and 760 nm, and a shoulder at 450 nm. These features are very similar to the ones

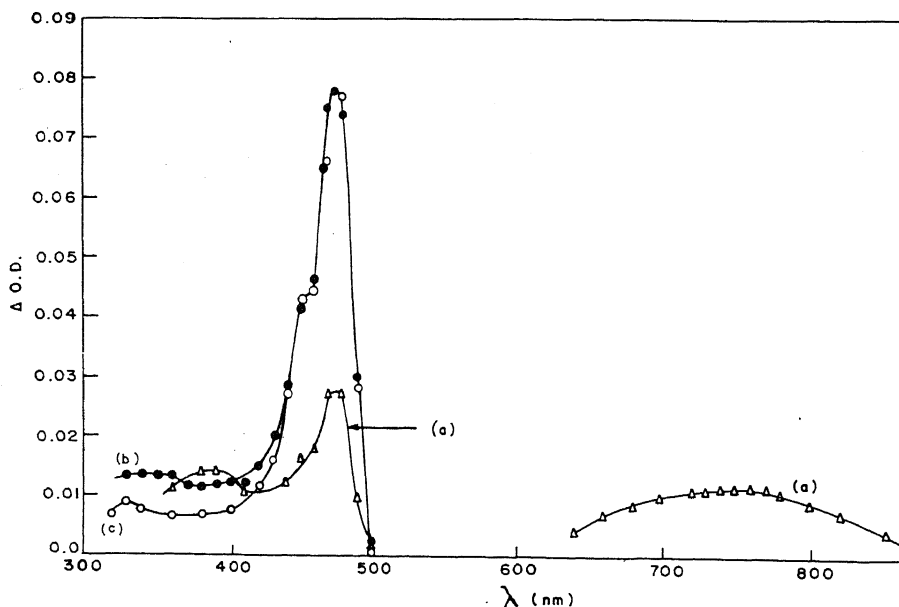
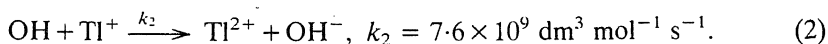
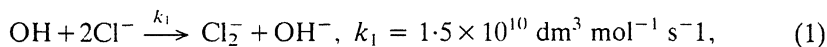


Figure 1. Absorption spectra of transient products formed by the reaction of OH (a), Cl_2 (b), and Ti^{3+} (c) in e -pulse irradiated aqueous thionine solutions at pH 1.7.

reported by Kamat and Lichtin (1982) and attributed by them to an equimolar mixture of semioxidized and semireduced forms of thionine formed by intermolecular electron transfer between ground and triplet excited thionine. In our system (O_2 -saturated acid medium), as noted above, the HO_2 radicals are inert, and reaction of thionine with the oxidising species (OH) can give rise to only the semioxidized thionine species. Although OH is a very strong oxidant ($E^\circ = 2.8$ V; Buxton 1982), it can also bring about reactions other than oxidation such as addition to the heteroaromatic ring of thionine, abstraction of hydrogen atom etc. Hence we were led to try more specific and known one-electron oxidants (Bonifacic and Asmus 1976) viz. Cl_2^- , Tl^{2+} , Br_2^- , N_3 etc.

In oxygen saturated acidic solutions OH radicals can be quantitatively converted to Cl_2^- and Tl^{2+} via reactions:



The transient spectra observed on pulsing acidic solutions containing $5 \times 10^{-5} \text{ mol dm}^{-3}$ thionine and $0.01 \text{ mol dm}^{-3} Cl^-$ or $0.002 \text{ mol dm}^{-3} Tl^+$ are shown in figure 1 (curves b and c). These spectra show a maximum at $\sim 480 \text{ nm}$ and a shoulder at $\sim 450 \text{ nm}$, but no broad maxima in the 760 nm region, and are remarkably similar to the semioxidized thionine species reported by Kamat and Lichtin (1982). Further evidence to suggest the generation of the species by reaction with Cl_2^- can be seen in figure 2 which depicts the time resolved transient

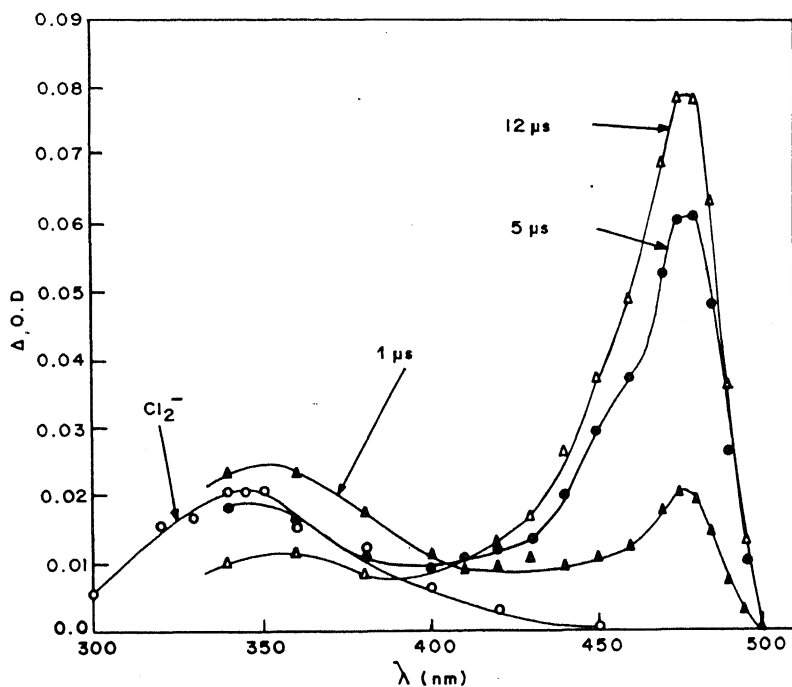


Figure 2. Time resolved absorption spectra of semioxidized thionine species formed by the reaction of Cl_2^- (Δ —1 μ s; $\bullet$ —5 μ s; $\triangle$ —12 μ s after the e -pulse) and the absorption spectrum of Cl_2^- radical ($\circ$ —1 μ s after the e -pulse).

spectra of electron beam pulsed O_2 saturated acidic solutions containing $0.01 \text{ mol dm}^{-3} \text{Cl}^-$ and $5 \times 10^{-5} \text{ mol dm}^{-3}$ thionine. It is seen that with passage of time the Cl_2^- absorption peak at 345 nm progressively diminishes in intensity accompanied by a simultaneous increase in the 480 nm peak from the product. The transient signals at 345 nm due to the Cl_2^- species in the absence and presence of thionine in oxygen-saturated acidic solution containing $0.01 \text{ mol dm}^{-3} \text{Cl}^-$ are given in figure 3. From this it is seen that Cl_2^- decay becomes appreciably faster in the presence of thionine, indicating the reaction of Cl_2^- with that compound. From the kinetics of build-up of product transient absorbance at 480 nm which was found to be pseudo first-order with respect to thionine concentration, a value of $3.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$ was calculated for the rate constant of this reaction.

The Ti^{2+} species has an absorption spectrum which overlaps with that of thionine; hence the effect of the latter on its decay could not be studied. The product transient build-up at 480 nm was again found to be pseudo first-order with respect to thionine concentration and a value of $3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$ was obtained for the bimolecular rate constant.

Reaction of Cl_2^- or Ti^{2+} cannot be studied in the neutral pH region, because the reaction of Cl^- with OH^- is extremely slow at $\text{pH} > 3$ (Anbar and Thomas 1964) whereas Ti^{2+} hydrolyses to $\text{Ti}(\text{OH})^+$ and $\text{Ti}(\text{OH})_2$ in less acidic media; $pK_1 = 4.6$, $pK_2 = 7.7$ (Bonifacic and Asmus 1976b). One-electron oxidants useful in the higher pH region are N_3^- , Br_2^- , I_2^- which can be generated by electron beam pulsing of N_2O saturated aqueous solutions of NaN_3 , KBr and KI , respectively, via reactions:

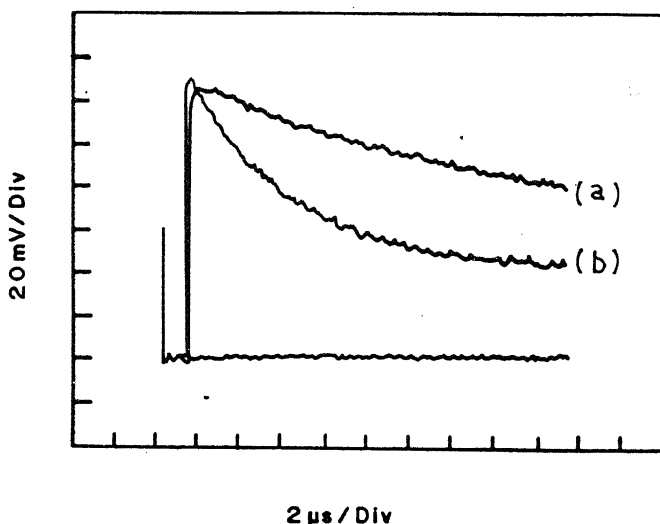
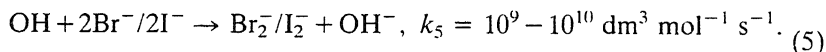
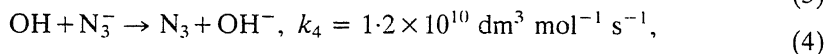
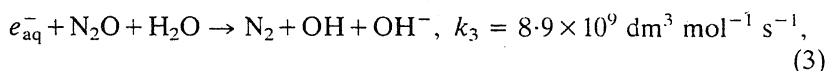


Figure 3. Decay of Cl_2^- radical absorption ($\lambda = 345 \text{ nm}$) in the absence (a) and presence (b) of thionine ($5 \times 10^{-5} \text{ mol dm}^{-3}$), $\text{pH} 1.7$.

N_2O saturated aqueous solution (pH 6–10) containing 0.05 mol dm^{-3} KBr or KI and $10^{-4} \text{ mol dm}^{-3}$ thionine on e -beam pulsing did not reveal the formation of any transient light absorbing species indicating that Br_2^- and I_2^- are not able to oxidize thionine. However, N_2O saturated solutions containing $0.005 \text{ mol dm}^{-3}$ NaN_3 and $10^{-4} \text{ mol dm}^{-3}$ thionine did produce transient light absorbing species on e -beam pulsing. These had features in the 400–500 nm region characteristic of the semioxidized thionine species. Hence it is inferred that N_3 radicals are able to oxidize thionine. Typical absorption spectra of product species are given in figure 4. The transient spectra obtained by the Ti(II) reaction with thionine at pHs 5.8 and 9.6 (figure 4) were similar to those obtained by N_3 reaction at pHs 4.8 and 9.6, supporting the above observation.

In order to evaluate the pK of the semioxidized thionine species, transient absorbance at 480 nm of e -beam pulsed solutions were measured as a function of pH. Because of the fact that (1) is very slow above pH 3 and N_3^- has a $pK = 4.7$, the HN_3 species present at $\text{pH} < 4$ being rather unreactive towards OH, a single matrix could not be employed for the entire pH region. Below pH 3, O_2 -saturated 0.01 mol dm^{-3} NaCl was used, whereas above pH 4, the matrix employed was N_2O saturated 0.05 mol dm^{-3} NaN_3 . The net G -values for the oxidizing species in these two matrices are 2.8 and 5.5, respectively; hence the measured absorbances were normalized to unit G -value of the oxidizing species and plotted (figure 5). The plot clearly reveals two inflexion points, corresponding to $pK = 6.9$ and 8.3. It is difficult to infer from this figure whether there is one more pK at more acidic pH. This region was investigated by using Ti(II) as the oxidizing species. The results plotted in figure 5 clearly reveal the presence of another pK at 4.3 for the

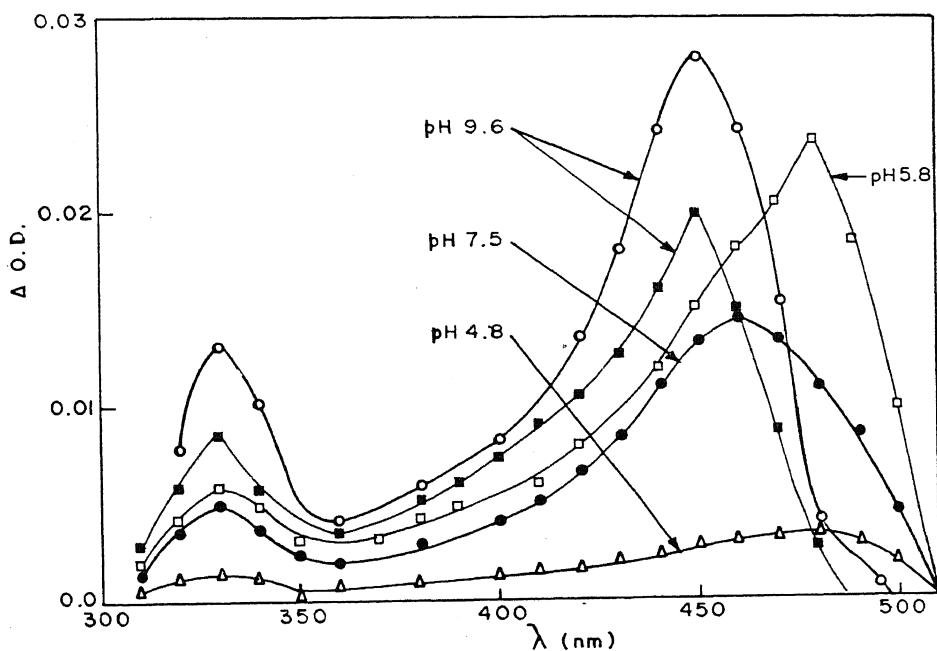


Figure 4. Absorption spectra of different conjugate acid-base forms of semioxidized thionine species produced by the reaction of N_3 (Δ , $\bullet$, $\circ$) and Ti(II) ($\square$, $\blacksquare$).

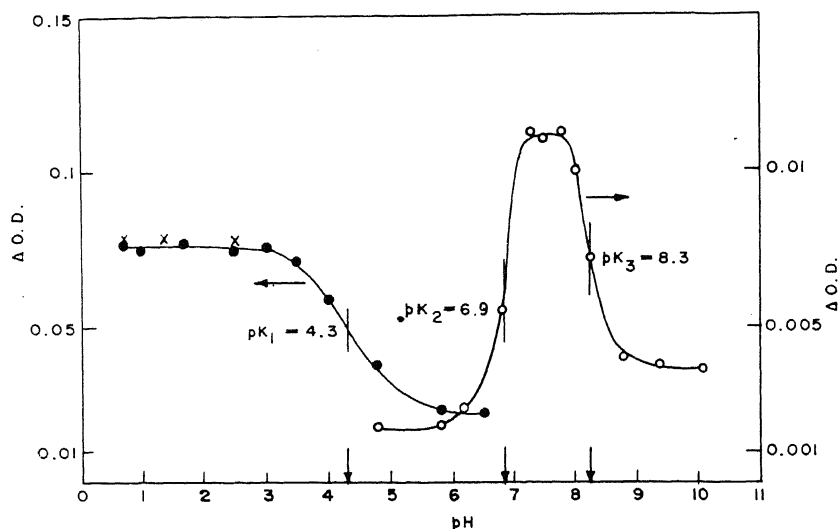


Figure 5. Absorbance changes with pH at 480 nm for the semioxidized thionine species formed by Cl_2 (x), Tl(II) (●) and N_3 (○).

semioxidized thionine species. That this is a genuine pK for this species and not an artefact due to the different hydrolytic forms of Tl(II) with pK at 4.6 is supported by the following observations. First, both at pH 2.5 and 5.8, the two forms of Tl(II) were found to oxidize thionine with the same rate constant of $3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Hence the extent of oxidation by Tl(OH)^+ form cannot be expected to be very much less than that by the Tl^{2+} form. Bonifacic and Asmus (1976b) have reported that the oxidizing efficiency of Tl(OH)^+ is $\sim 85\%$ of that of Tl^{2+} in the case of Me_2S_2 whereas Tl(OH)_2 form has only 20% efficiency. In another system (Moorthy *et al* 1987) semioxidized riboflavin, which has no pK in this region, exhibited no change in the transient absorption as a function of pH on pulsing O_2 -saturated solutions containing Tl^+ , thus indirectly showing that the inflexion observed in the case of thionine is not an artefact. The λ_{max} and ϵ_{max} values of the different conjugate acid-base forms are given in table 1.

Although the spectrum of the product species formed from thionine by reaction with OH radicals has some resemblance to that of the semioxidized species, further experiments revealed that the two species are quite different. Thus the absorbance of the OH reaction product at 770 and 480 nm changes with pH (figure 6) in a manner quite different from the one observed in the case of the semioxidized species (figure 5). Also the spectra at pH 9.5 and 3 observed for the OH reaction product (figure 7) are quite different from those of the semioxidized species (figures 2–3). Although the 770 nm band is indicative of the semireduced thionine species, this band present in the spectrum of the OH reaction product cannot be ascribed to the semireduced species for the following reason. In the pulse radiolytic reduction studies on thionine reported earlier (Guha *et al* 1987), the 770 nm band was totally absent in the spectra in alkaline pHs, whereas this band is observed in the case of OH reaction product at all pHs. The absorption spectrum at pH 9.5 appears to be that due to a mixture of species.

Table 1.

Protonated form of semioxidized thionine	pH	$\lambda_{\max}$ (nm)	Corrected ϵ ($10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
TH_2^{3+}	1.7	480	3.5
TH^{2+}	5.8	480	1.35
T^+	7.5	460	2.8
$\text{T}(-\text{H}^+)$	9.6	450	5.3

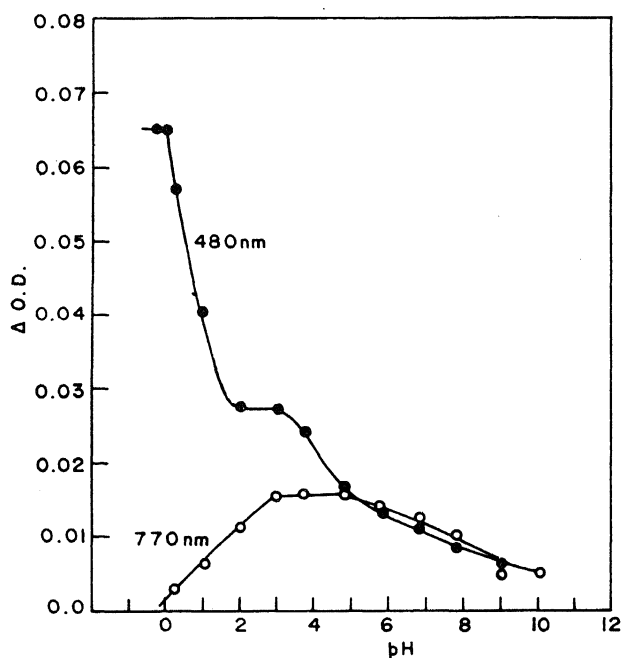


Figure 6. Absorbance changes with pH for the OH-reaction product of thionine at 770 and 480 nm.

4. Discussion

The standard potentials for reduction of the various one-electron oxidants as reported in the literature are summarized in table 2. Generally the more positive this potential, the stronger the species is expected to be as an oxidizing agent. The rates and efficiencies of oxidation are expected to follow this trend. Although there are divergent values for the potential of the N_3/N_3^- couple, the lower value is supported by recent equilibrium pulse radiolysis experiments and confirmed by cyclic voltammetry (Alfassi *et al* 1987). Our observation that thionine is oxidizable by Cl_2^- , Ti^{2+} and N_3 but not by I_2^- would place the potential of the semioxidized thionine/thionine couple between +2.3 and +1.0 volt. From the normalized

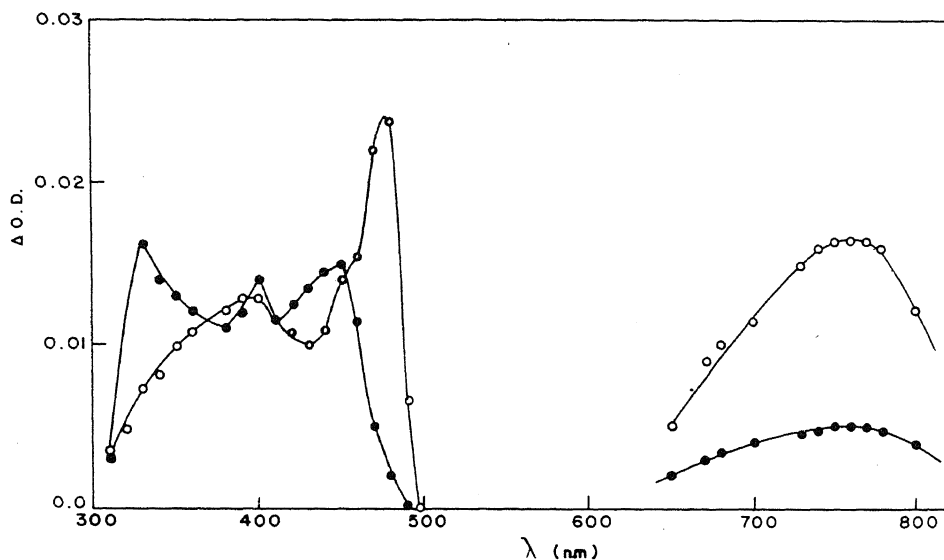


Figure 7. Absorption spectra of OH-reaction product at pH 3 (○) and pH 9.6 (●).

Table 2. One-electron oxidation potential of various radicals.

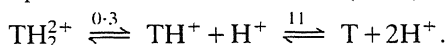
Radical	$E^{\circ'}$ (V vs. NHE)	Reference
Ti^{2+}	2.22	Schwarz <i>et al</i> (1974)
Cl_2^-	2.3	Henglein (1980)
Br_2^-	1.7	Henglein (1980)
I_2^-	1.0	Henglein (1980)
N_3	1.32	Alfassi <i>et al</i> (1987)

absorbance vs. pH curves (figure 5) for the semioxidized species generated by using different oxidant species, it would appear that the efficiency of N_3 for oxidizing thionine is considerably less than that of Cl_2^- , Ti^{2+} or $\text{Ti}(\text{OH})^+$, but is comparable to that of $\text{Ti}(\text{OH})_2$. (However, the rate constants of these oxidation reactions do not reflect this trend, being all $2\text{--}4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Hence the potential of the semioxidized thionine/thionine couple is likely to be close to but more positive than that of the N_3/N_3^- couple (table 1), i.e. 1.3 V, as the efficiency of this couple in oxidizing thionine is considerably less than 50%. Considering this, the inability of Br_2^- to oxidize thionine would at first sight suggest that the potential of the $\text{Br}_2^-/2\text{Br}^-$ couple must be much lower than 1.7 volts. However the equilibrium pulse radiolysis experiments by Alfassi *et al* (1987) between the N_3/N_3^- and $\text{Br}_2^-/2\text{Br}^-$ couples lead to the value of 1.3 V for the former on the basis of a value of 1.63 V for the latter couple. Hence the inability of Br_2^- to oxidize thionine appears to be inexplicable on the basis of redox potentials alone.

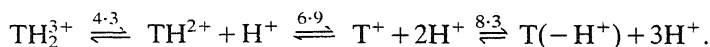
The extinction coefficient of semioxidized thionine at the λ_{max} of 480 nm at pH 1.7 (evaluated by assuming the extent of oxidation of thionine by Ti^{2+} or Cl_2^- at this pH

to be 100%) is $35,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. This value is considerably higher than the one reported by Kamat and Lichtin (1982). It may be noted that their estimate is based on the assumption that under photochemical excitation intermolecular electron transfer is the only route for the formation of semioxidized and semireduced thionine. If, as reported by Somer and Green (1973), photoexcited thionine, particularly at high concentrations, is reducible by water also, contributing to an additional yield of semithionine, the extinction coefficient based on the above assumption is expected to be lower. From our results the extent of oxidation of thionine by N_3 was found to be $\sim 18\%$; this value is made use of to evaluate the extinction coefficient of semioxidized thionine at the λ_{max} values of its spectra at pH 9.6 and 7.5, respectively. The value for the other two forms were calculated on the basis of 100% efficiency of oxidation by $\text{Ti}(\text{OH})^+$ and Cl_2^- .

The present experiments do not throw any light on the site of oxidation of thionine; it may be the heteroaromatic thiazine ring. In neutral solutions the molecule is present as the monocation (TH^+) and has pK values of 0.3 and 11:



As the semioxidized species is electron deficient, it can be expected to lose protons more readily than the parent thionine. Hence the pK values of the former are assigned as follows:



Acknowledgements

We express our sincere appreciation of the encouragement and support from Drs J P Mittal and R M Iyer, and of useful discussions with Shri D B Naik.

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Electronic structure of biopolymers — solid state aspects

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MS received 28 September 1987; revised 3 December 1987

Abstract. *Ab initio* results of the electronic structure and conduction properties of both periodic and aperiodic DNA and protein models are reviewed. Band structure results of the periodic systems are obtained on the basis of the *ab initio* Hartree-Fock crystal orbital method. The electronic density of states (DOS) of the multicomponent periodic and aperiodic polypeptide chains, and of single-stranded periodic and aperiodic DNA, on the other hand, are determined using the *ab initio* matrix block negative factor counting technique. Large values of the fundamental energy gap obtained for all the systems studied rule out the possibility of intrinsic conduction in them. The DOS curves of aperiodic DNA and polypeptide chains, in contrast to those of corresponding periodic systems, are found to consist of relatively broader regions of allowed energy states with a few small gaps in between. The study of the localization properties of the lowest unoccupied energy levels in the conduction band region of aperiodic polypeptide chains indicates that these wavefunctions are highly localized. In the light of these results, the possibility of charge transport through hopping conduction in proteins under the assumption of charge transfer to the polypeptide chains is discussed. Finally, how the correlation effects could be considered in an approximate way for these biopolymers is outlined.

Keywords. Biopolymer electronic structure; periodic polypeptide; aperiodic polypeptide; *ab initio* H-F crystal orbital method; hopping conduction in proteins.

1. Introduction

Biopolymers such as proteins and DNA play a role of fundamental importance in life processes. Proteins are structurally the most important building stones of the living cell and in the form of enzymes catalyse various biochemical processes. DNA, on the other hand, is the carrier of genetic information, and through the RNA determines the sequence of amino acids in different proteins and with this their secondary and tertiary structures. In order to understand various physical and chemical properties (such as charge distributions and reactivity indices of the constituent molecules, density of states, ESR, electronic and vibrational spectra, different transport properties etc.) of these biopolymers, and on their basis their biological functions, one needs to know their electronic structure fairly well.

The quantum mechanical investigation of the electronic structure of these biopolymers is a very challenging task due to the complexity of these systems. Both

proteins and DNA have large molecules as their units and the sequence of these units is aperiodic. DNA-B is composed of two antiparallel right handed helices of polydeoxyribonucleotides which in DNA-B form a double helix (Watson and Crick 1953). In each strand of the helix four nucleotide bases adenine (A), thymine (T), guanine (G) and cytosine (C) form stacks and have an aperiodic sequence, though the corresponding sugar-phosphate backbones in the DNA helices are periodic. The allowed base pairs in the two right handed antiparallel strands are A-T and G-C. Though the stereo structure of DNA is fairly well known today, the actual sequence of the bases in different DNA molecules is still largely unknown. Proteins, on the other hand, are composed of one or more polypeptide chains (made up from 20 different amino acid residues) that for parts of their lengths can be folded in an apparently random way or form regular β -pleated sheet or α -helical structures. The sequence of amino acids in a great number of proteins is known, though the conformations of only a few smaller protein molecules have been determined with the aid of x-ray diffraction. Further, under biological conditions there are ions and water molecules which make the determination of the electronic structure of these biopolymers even more difficult. In view of all this, it is not possible to determine the electronic structure of proteins and DNA in one step. We have, therefore, to proceed stepwise using a combination of various techniques with rather large scale computations.

(1) As a first step to approximate the electronic structure of proteins and DNA, we can start with the band structure calculations of periodic protein (periodic polypeptides) and periodic DNA (nucleotide base stacks, poly base-pairs, homopolynucleotides) models using self-consistent crystal orbital methods (see §2).

(2) As a next step towards more realistic models, one has to use the theory of disordered systems to treat aperiodicity present in both proteins and DNA. Direct SCF methods cannot be used in view of the large size and the random arrangement of their units.

(3) Since the real biological situation in the case of these biopolymers also involves solvation and ions, one has also to study the effect of this environment on the band structure (in the case of periodic chains), and on the electronic density of states (DOS) distribution (in the case of aperiodic chains). This may be achieved by constructing an effective potential of the environment (Otto *et al* 1982).

(4) Finally one should also take into account (using a better basis set) the major part of electronic correlation (Suhai and Ladik 1982; Ladik 1983) in the case of both periodic and aperiodic protein and DNA chains.

(5) Having executed the above steps in the case of both proteins and DNA, one is in a position to compute different properties (such as spectra, transport properties, magnetic and mechanical properties etc.) of these biopolymers.

(6) It is also very important to treat interactions between proteins and DNA. Nucleohistones – the complexes formed between proteins and DNA – are of great interest in molecular biology. It is believed (Ladik *et al* 1978) that the change in interactions between these biopolymers caused by chemical carcinogens binding to DNA and/or proteins may be one of the determinant steps in the mechanism of tumour development.

In this article the *ab initio* results of the electronic structure of proteins and DNA are reviewed. Section 2 deals with the methods used in the investigation of electronic structure of both periodic and aperiodic biopolymer chains. In §3 are

given the band structure results of periodic protein and DNA models. The results of the electronic structure and conduction properties of aperiodic proteins and DNA are reviewed in §4. The treatment of electron correlation effects in these biopolymers is considered in §5.

2. Methods

2.1 *Ab initio* crystal orbital method

The band structures of periodic DNA and protein models can be determined on the basis of the *ab initio* Hartree-Fock crystal orbital method. This method results from the Hartree-Fock-Roothaan (Roothaan 1951) method for finite molecules by including periodic boundary conditions (Born and Von Karman 1912) and has been derived in full detail simultaneously and independently by Del Re *et al* (1967) and Andre *et al* (1967). Here we give only the most important equations of this method.

The total wavefunction of a polymer in the crystal orbital method is given by a Slater determinant with a doubly-filled Bloch function $\psi_n^k(\mathbf{r})$ which represents a one-electron state with quasi-momentum k in band n . The Bloch functions are represented as a linear combination of Bloch basis orbitals $\phi_a^k(\mathbf{r})$

$$\psi_n^k(\mathbf{r}) = \sum_{a=1}^{\nu} C_{an}^k \phi_a^k(\mathbf{r}) \quad (1)$$

where ν is the number of basis orbitals per unit cell and the Bloch basis orbitals $\phi_a^k(\mathbf{r})$ are the linear combinations of symmetry-adapted atomic orbitals $\chi_a^j(\mathbf{r})$,

$$\phi_a^k(\mathbf{r}) = N^{-1/2} \sum_j \exp(ikja) \chi_a^j(\mathbf{r}). \quad (2)$$

N is the number of unit cells, a is the translational period of the polymer and $\chi_a^j(\mathbf{r}) = \chi_a^j(\mathbf{r} - \mathbf{R}_a - ja)$ is an atomic orbital in the unit cell at $\mathbf{R}_a + ja$.

Applying the Born-Oppenheimer electronic Hamiltonian and using the Ritz variation procedure with the orthonormality equation $\langle \psi_n^k(\mathbf{r}) | \psi_m^k(\mathbf{r}) \rangle = \delta_{nm}$, the following complex pseudo-eigenvalue problem is obtained

$$F^k C_n^k = \varepsilon_n^k S^k C_n^k, \quad (3)$$

where the k -dependent Fock and overlap matrix elements are defined in the usual way as the lattice sums

$$F_{ab}^k = \sum_j \exp(ikja) f_{ab}^{0j}, \quad (4)$$

$$S_{ab}^k = \sum_j \exp(ikja) s_{ab}^{0j}. \quad (5)$$

R_j is a lattice vector in a direct space pointing from the reference cell to cell j . Lower indices on f and s refer to basis functions, upper indices to cell positions. Elements s_{ab}^{0j} are defined as

$$s_{ab}^{0j} = \langle \chi_a^0(\mathbf{r}) | \chi_b^j(\mathbf{r}) \rangle. \quad (6)$$

Fock matrix element f_{ab}^{0j} in direct space is defined as

$$f_{ab}^{0j} = h_{ab}^{0j} + g_{ab}^{0j}, \quad (7)$$

$$h_{ab}^{0j} = -\frac{1}{2} \langle \chi_a^0(r) | \nabla_r | \chi_b^j(r) \rangle - \sum_h \sum_A \left\langle \chi_a^0(r) \left| \frac{Z_A}{r - R_A - R_h} \right| \chi_b^j(r) \right\rangle, \quad (8)$$

$$g_{ab}^{0j} = \sum_h \sum_l \sum_c \sum_d p_{cd}^{hl} \left[2 \begin{pmatrix} 0 & j \\ a & b \end{pmatrix} \begin{pmatrix} h & l \\ c & d \end{pmatrix} - \begin{pmatrix} 0 & h \\ a & c \end{pmatrix} \begin{pmatrix} j & l \\ b & d \end{pmatrix} \right]. \quad (9)$$

The electronic density matrix elements p_{cd}^{hl} between AO's c and d in cells h and l are defined by summation over all occupied states (k, n) in the first Brillouin zone (BZ) as

$$p_{cd}^{hl} = \sum_k \sum_{n \text{ occ}} \exp[-ik(R_h - R_l)] C_{cn}^{k*} C_{dn}^k, \quad (10)$$

and the two-electron integrals in (9) are defined as

$$\begin{pmatrix} 0 & j \\ a & b \end{pmatrix} \begin{pmatrix} h & l \\ c & d \end{pmatrix} = \int d\mathbf{r}_1^3 \int d\mathbf{r}_2^3 \chi_a^0(\mathbf{r}_1) \chi_b^j(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_c^h(\mathbf{r}_1) \chi_d^l(\mathbf{r}_2). \quad (11)$$

Using the above equations, the total energy per unit cell may be expressed as

$$E = \frac{1}{2} \sum_j \sum_a \sum_b (h_{ab}^{0j} + f_{ab}^{0j}) p_{ab}^{0j} + \frac{1}{2} \sum_j \sum_A \sum_B \frac{Z_A Z_B}{(R_A - R_j - R_B)}. \quad (12)$$

One has to solve the above equations at a number of k points to be able to construct the matrices p_{cd}^{hl} for the next iteration step. Using appropriate numerical techniques, it is usually enough to consider 6–8 k points between 0 and $\pi/2$ [$\varepsilon^{(k)} = \varepsilon^{(-k)}$] to obtain consistent results.

It needs to be noted that by applying the *ab initio* CO method only ground state properties such as equilibrium geometries, total energy per unit cell, force constants etc. can be evaluated.

2.2 Negative factor counting (NFC) technique for the treatment of quasi-one-dimensional disordered systems

One of the major problems encountered in the investigation of the electronic structure of proteins and DNA is the treatment of aperiodicity in these systems. Proteins and DNA have a strong aperiodicity due to the random sequence of the twenty amino acid residues and the four nucleotide bases, respectively. The electronic DOS of quasi-one-dimensional disordered systems can be determined using negative factor counting (NFC) method based on Dean's negative energy eigenvalue theorem (Dean 1972). There are two versions of this method: (1) a simple NFC method in which one obtains the DOS of an aperiodic polymer for a single band at a time, and (2) a matrix block NFC method which is relatively more sophisticated and by which one can determine the total DOS coming from all the bands (both valence and conduction).

2.2a Simple NFC method: In the simple NFC method, in order to determine the electronic DOS of a multicomponent quasi-one-dimensional system, one writes down a Huckel determinant (Huckel 1931)

$$|H(\lambda)| = \begin{vmatrix} \alpha_1 - \lambda & \beta_{1,2} & 0 & 0 & \dots & \dots & 0 \\ \beta_{1,2} & \alpha_2 - \lambda & \beta_{2,3} & 0 & & & \\ & & & & & & \\ 0 & \beta_{2,3} & \alpha_3 - \lambda & \beta_{3,4} & & & \\ \vdots & & & & & & \\ \vdots & & & & & & \\ \vdots & & & & & & \\ \vdots & & & & & & \\ \vdots & & & & & & \\ 0 & & & \beta_{N-1,N} & & & \alpha_{N-\lambda} \end{vmatrix} = 0 \quad (13)$$

of an aperiodic chain consisting of N units. The determinant is tridiagonal due to the fact that only first neighbour interactions are taken into account (tight binding approximation). In (13) α_i ($i = 1, 2, \dots, N$) and $\beta_{i-1,i}$ ($i = 2, 3, \dots, N$) are the diagonal and off-diagonal matrix elements, respectively, of an effective one-electron Hamiltonian and λ is its eigenvalue.

The tridiagonal determinant can be easily transformed into a didiagonal one with the help of successive Gaussian eliminations. Thus the equation

$$|H(\lambda)| = \prod_{i=1}^N (\lambda_i - \lambda), \quad (14)$$

can be rewritten as

$$|H(\lambda)| = \prod_{i=1}^N \varepsilon_i(\lambda), \quad (15)$$

where the diagonal elements of the didiagonal determinant are given by the simple relation

$$\varepsilon_i(\lambda) = \alpha_i - \lambda - \beta_{i-1,i}^2 / \varepsilon_{i-1}(\lambda), \quad i = 2, 3, \dots, N, \quad (16)$$

$$\varepsilon_1(\lambda) = \alpha_1 - \lambda. \quad (17)$$

Since (14) and (15) are equal, it is easy to see that for a given λ value the number of eigenvalues smaller than λ has to be equal to the number of negative $\varepsilon_i(\lambda)$ factors in (15). By giving λ different values throughout the spectrum and taking the difference of the number of negative $\varepsilon_i(\lambda)$'s belonging to consecutive values one can obtain the DOS for an aperiodic polymer chain to any desired accuracy.

In actual calculations, the diagonal α_i and the off-diagonal $\beta_{i-1,i}$ matrix elements of the secular determinant are determined from the corresponding band structure results of each component constituting the polymer chain (i.e. 20 in the case of proteins and 4 in the case of DNA). For a given band, α_i of a component is taken to be the mid-point (or weighted mid-point) of the corresponding band. Assuming the dispersion of the band to be given by the simple relation

$$\varepsilon_A(k) = \alpha_A(k) + 2\beta_{A,A} \cos(ka). \quad (18)$$

$\beta_{A,A}$ is taken to be one-fourth of the band width if the same component A is repeated. If on the other hand, component A is followed by component B , then the off-diagonal matrix element $\beta_{A,B}$ is assumed to be given by the simple relation

$$\beta_{A,B} = \frac{1}{2} (\beta_{A,A} + \beta_{B,B}). \quad (19)$$

2.2b Matrix block NFC method: In contrast to the simple NFC method which assumes one orbital per unit in the polymer chain, the matrix block NFC method can be applied for an arbitrary number of orbitals per unit. In this case, therefore, instead of a tridiagonal, we have a triblock diagonal secular determinant

$$|H(\lambda)| = \begin{vmatrix} A_1 - \lambda S_1 & B_{1,2} - \lambda Q_{1,2} & 0 & \dots & \dots \\ B_{1,2}^T - \lambda Q_{1,2}^T & A_2 - \lambda S_2 & B_{2,3} - \lambda Q_{2,3} & 0 & \dots \\ 0 & \dots & \dots & \dots & \dots \\ \vdots & & & & A_N - \lambda S_N \end{vmatrix} = 0. \quad (20)$$

Here A_i and $B_{i,i+1}$ are the diagonal and off-diagonal blocks of the Fock matrix, and S_i and $Q_{i,i+1}$ the corresponding blocks of overlap matrix. It can be shown that (20) can be brought into the form

$$|H(\lambda)| = \det S \det (\tilde{F} - \lambda I) = \left(\prod_{i=1}^n s_i \right) \left[\prod_{j=1}^n (\lambda_j - \lambda) \right], \quad (21)$$

where $\tilde{F} = S^{-1/2} F S^{1/2}$. The s_i are the eigenvalues of S and the λ_j are the roots of the generalised eigenvalue equation

$$F c_j = \lambda_j S c_j. \quad (22)$$

As in the case of the simple NFC method, here also the triblock diagonal determinant $|F - \lambda S|$ can be easily brought into a didiagonal form by applying the successive Gaussian elimination procedure. One obtains in this way for the new diagonal blocks,

$$U_i(\lambda) = A_i - \lambda S_i - (B_{i,i+1}^T - \lambda Q_{i,i+1}^T) U_{i-1}^T (B_{i,i+1} - \lambda Q_{i,i+1}), \quad (23)$$

with

$$U_1(\lambda) = A_1 - \lambda S_1. \quad (24)$$

Now if $U_{ik}(\lambda)$ stands for the k th eigenvalue of the diagonal matrix block $U_i(\lambda)$ defined by (23) and l_i is its dimension. Then

$$\begin{aligned} |F - \lambda S| &= |M(\lambda)| = \left(\prod_{i=1}^n s_i \right) \prod_{j=1}^n (\lambda_j - \lambda) \\ &= \prod_{i=1}^N \left(\prod_{k=1}^{l_i} U_{ik}(\lambda) \right), \quad n = \sum_{i=1}^N l_i. \end{aligned} \quad (25)$$

The matrices $U_i(\lambda)$ can be easily diagonalised for a given value of λ . The number of the negative $U_{ik}(\lambda)$ values has to be equal again to the number of those eigenvalues

λ_j which are smaller than the chosen λ value. Thus by changing λ , the whole spectrum can be scanned again and in this way the total DOS of the aperiodic chain can be obtained for all the bands to any desired accuracy.

For the application of the matrix block NFC method one requires, as a first step, the various Fock and overlap matrix blocks to construct a secular determinant, (20). These matrix blocks are obtained from the corresponding cluster studies (a cluster in the first neighbour interaction approximation consists of two interacting molecules) using the *ab initio* Hartree-Fock SCF LCAO method and represent interactions both within the unit and with the neighbouring unit, respectively. For a disordered chain containing P different components one has to study P^2 different clusters (e.g. in the case of a binary chain of two components A and B the four clusters to be studied are AA , AB , BA , BB). From the results of each cluster (say

AB where AB stands for the helix direction $\begin{smallmatrix} B \\ \uparrow \\ A \end{smallmatrix}$ the diagonal Fock and overlap

matrix blocks, representing interactions within the molecule A and the off-diagonal Fock and overlap matrix blocks representing interactions of molecule A with molecule B , are extracted. Thus 4 matrix blocks are used from each cluster. In the case of proteins and DNA, one, therefore, has to study 400 and 16 clusters, respectively, corresponding to 20 different amino acid residues and 4 nucleotide bases, thereby giving in all 1600 matrix blocks (in case of proteins) and 64 matrix blocks (in case of single stranded DNA). The elements of these matrix blocks are then required to be transformed to represent the various orientations of the aperiodic polypeptide and aperiodic DNA chains. In the case of DNA-B with 10 stacked bases in one helical turn (helical angle 36°), the elements of 64 matrix blocks are transformed nine times stepwise through a rotation of 36° thereby giving in all 640 matrix blocks which have the complete information about a single turn of the DNA-B helix. Similarly for the antiparallel β -pleated conformation of polypeptide chains (helical angle 180°), 1600 matrix blocks are to be rotated through 180° to give in all 3200 matrix blocks. Using these matrix blocks (3200 in case of proteins and 640 for DNA-B) one can set up the secular determinant for any pre-specified sequence of units in the case of proteins and DNA and determine the corresponding electronic DOS using matrix block NFC method.

3. Electronic structure of periodic protein and DNA models

3.1 Periodic protein models

3.1a *Homopolypeptides*: The band structure results of all the 20 homopolypeptides calculated on the basis of *ab initio* Hartree-Fock LCAO SCF CO method are given in table 1 (Otto *et al* 1986). The geometry of the amino acid residues representing the elementary unit cell has been built up using standard bond lengths and bond angles (Sutton 1958). The secondary structure of the elementary unit cell has been taken to be an antiparallel β -pleated sheet structure (Pauling *et al* 1951, see figure 1) – the exception being polyproline for which the structural parameters of polyL-proline I and II have been applied (Sasisekharan 1959; Traub and

Table 1. Band structure results of homopolypeptides in β -pleated sheet conformation. Table contains the energy minima ($E_{\min}$) and energy maxima ($E_{\max}$) of valence (n^*) and conduction ($n^* + 1$) bands, the band widths (ΔE) and the fundamental energy gap (E_{gap}) (all quantities are in eV).

Poly	Band	($E_{\min}$)	($E_{\max}$)	Band width (ΔE)	Fundamental gap (E_{gap})
Glycine (gly)	$n^* + 1$	2.591	4.166	0.575	15.777
	n^*	-12.579	-12.186	0.393	
Alanine (ala)	$n^* + 1$	3.722	4.395	0.673	15.776
	n^*	-12.288	-12.054	0.234	
Valine (val)	$n^* + 1$	2.751	3.329	0.578	14.671
	n^*	-12.096	-11.921	0.176	
Leucine (leu)	$n^* + 1$	5.606	6.863	1.157	10.824
	n^*	-5.241	-5.118	0.123	
Isoleucine (ileu)	$n^* + 1$	5.898	7.266	1.367	11.877
	n^*	-6.131	-5.979	0.152	
Serine (ser)	$n^* + 1$	4.265	4.996	0.731	15.366
	n^*	-11.176	-11.101	0.075	
Threonine (thr)	$n^* + 1$	4.002	4.601	0.599	15.266
	n^*	-11.328	-11.263	0.064	
Cysteine (cys)	$n^* + 1$	4.100	4.789	0.689	14.376
	n^*	-10.686	-10.636	0.050	
Methionine (met)	$n^* + 1$	3.319	4.025	0.706	13.846
	n^*	-10.544	-10.527	0.017	
Asparagine (asn)	$n^* + 1$	3.988	4.587	0.599	15.572
	n^*	-11.704	-11.584	0.120	
Glutamic acid (glu)	$n^* + 1$	3.208	3.229	0.021	15.388
	n^*	-12.478	-12.180	0.298	
Phenylalanine (phe)	$n^* + 1$	2.407	2.437	0.029	13.442
	n^*	-11.172	-11.035	0.137	
Tyrosine (tyr)	$n^* + 1$	2.232	2.867	0.084	12.677
	n^*	-10.388	-10.346	0.042	
Tryptophan (try)	$n^* + 1$	1.847	1.860	0.013	11.703
	n^*	-9.877	-9.856	0.021	
Aspartic acid (asp)	$n^* + 1$	3.169	3.178	0.019	15.057
	n^*	-12.109	-11.898	0.211	
Glutamine (gluNH ₂)	$n^* + 1$	3.028	3.712	0.684	15.245
	n^*	-12.238	-12.217	0.021	
Arginine (arg)	$n^* + 1$	3.599	4.237	0.638	14.134
	n^*	-10.537	-10.537	0.000	
Histidine (his)	$n^* + 1$	3.222	3.619	0.397	13.507
	n^*	-10.301	-10.285	0.016	
L-proline I (pro)	$n^* + 1$	3.763	4.251	0.488	15.080
	n^*	-11.583	-11.317	0.265	
L-proline II (pro)	$n^* + 1$	4.444	4.818	0.374	15.294
	n^*	-11.207	-10.850	0.357	

Shmueli 1963). The computations were carried out using Clementi's $7s$, $3p/9s$, $5p/2s$, $1p$ minimal basis set (Clementi *et al* 1977) taking into account interactions up to the second neighbour. All the multicentre two-electron integrals larger than the threshold value of 10^{-8} a.u. have been calculated.

Table 1 contains both minima and maxima of the valence (n^*) and conduction ($n^* + 1$) bands, band widths and fundamental energy gap values of all the

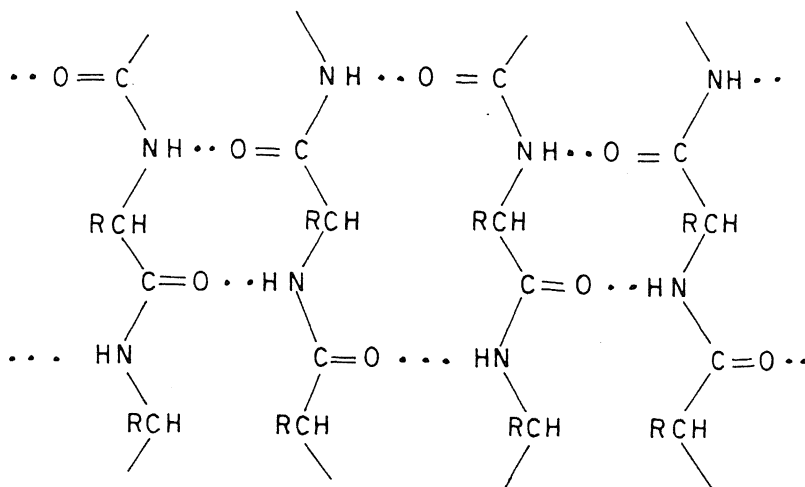


Figure 1. The β -pleated polypeptide structure.

homopolypeptides. The energy gap values range from 8.329 eV [poly(lys)] to 15.776 eV [poly(gly)]. The large values of the energy gap suggest that homopolypeptides in their pristine state are expected to be insulating. It needs to be pointed out here that the Hartree-Fock method overestimates the band gap values due to the neglect of the correlation effects and the use of the minimal basis set. With the use of better basis sets and the consideration of correlation effects, the calculated band gap values are expected to decrease as has been observed earlier in the case of *trans*-polyacetylene (Suhai 1983a) where the initially determined band gap value of 8.882 eV for STO-3G basis decreases to 2.980 eV through the use of 6-31G** basis and the consideration of correlation effects in the Moeller-Plesset form of many body perturbation theory in second order (Moeller and Plesset 1934). The band gap values obtained with the minimal basis set, however, correctly reproduce the trend in the experimental band gap values as has been shown in the case of heterocyclic polymers and their derivatives (Bakhshi *et al* 1987c; Bakhshi and Ladik 1987).

The lowest ionization potential (IP) values (corresponding to the top of the valence band) decrease with an increase in the number of methylene groups and aromatic rings in the side chains of the amino acid residues. Poly(glu) (12.217 eV) has the largest IP whereas poly(lys) (5.118 eV) has the smallest. It means that homopolypeptides with methylene groups or aromatic rings in the side chains have a relatively greater tendency to form conductive materials on doping with electron acceptors (*p*-doping). In contrast to the IP values, the electron affinity (EA) values (corresponding to the bottom of the conduction band region) which are a measure of the tendency of the polymer to form conductive materials on doping with electron donors (*n*-doping) show a less systematic trend with the values ranging from 0.458 eV [poly(lys)] to 5.898 eV [poly(ileu)].

Table 2 contains the *ab initio* band structure results of poly(gly), poly(ala) and poly(ser) in the α -helical conformation (Otto *et al* 1986). Comparison of these results with the corresponding β -pleated sheet structure results shows that for all the three systems, the fundamental energy gap in the α -helical conformation is smaller than that in the β -pleated sheet conformation. As is evident from this table, the position of the valence band is shifted to higher energies in the case of α -helical

Table 2. Band structure results of poly(gly), poly(ala) and poly(ser) in α -helical conformation. Symbols carry the same meaning as in table 1.

Poly	Band	$E_{\min}$	$E_{\max}$	ΔE	E_{gap}
Gly	$n^* + 1$	3.416	3.934	0.518	15.362
	n^*	-12.056	-11.947	0.109	
Ala	$n^* + 1$	3.394	3.704	0.310	14.741
	n^*	-11.393	-11.347	0.044	
Ser	$n^* + 1$	2.582	2.781	0.199	14.459
	n^*	-11.880	-11.877	0.003	

poly(gly) and poly(ala) but to lower energies in the case of poly(ser). The conduction bands of all the three α -helical homopolypeptides, on the other hand, are shifted to higher energies as compared to those of β -pleated structures.

3.1b Polydipeptides: *Ab initio* band structure results of the two polydipeptides poly(gly-ala) and poly(gly-ser) in both α -helical and β -pleated sheet conformations are given in table 3. As in the case of homopolypeptides, here too the fundamental energy gap values of the polydipeptides in α -helical conformation are smaller than those in β -pleated conformation, though in both cases the energy gap values are too large to allow intrinsic semiconductivity. It is interesting to note that in both conformations, the bands (both valence and conduction) of the polydipeptides are much narrower than those of the corresponding homopolypeptides constituting the dipeptide. The explanation is that in the case of polydipeptides, a small level splitting is caused (as one knows from simple perturbational theoretical arguments) due to the fact that different types of units always interact as first neighbours whereas in the case of homopolypeptides, the same unit is repeated throughout the polymer chain. Similar decrease in band widths in the case of poly(gly-ala), poly(gly-ser) and poly(ala-ser), relative to poly(gly), poly(ala) and poly(ser), has been observed by Suhai *et al* (1980) on the basis of all valence electron MINDO crystal orbital method in its MINDO/3 parametrization (Dingham *et al* 1975).

Direct SCF calculation of the polydipeptides of type poly(ser- m -gly) chains (where $m = 1, 2$ and 3) are not possible because of the large size of the unit cell. The knowledge of the band structure results of these chains, on the other hand, is necessary for understanding the effect of change of concentration of a component on the electronic structure of polydipeptides. The results of the electronic DOS of 300-unit long periodic poly(ser- m -gly) chains calculated on the basis of *ab initio* matrix block NFC method are shown in figures 2 and 3, respectively. In the case of poly(ser-gly) chain, the two highest filled bands, around 11.6 and 12.4 eV, can be assigned to ser and gly units, respectively (see the valence band positions of poly(gly) and poly(ser) in table 1). The widths of these two bands in comparison to those of homopolypeptides poly(gly) and poly(ser) are however considerably reduced. The reasons for this narrowing of bands have already been given. Comparison of the electronic properties of poly(gly-ser) chain obtained with the NFC method with those obtained using the crystal orbital method (table 3) shows that the agreement between the two methods is fairly good.

In the case of poly(ser-gly-gly) chains, the three highest occupied bands belong to one ser and two gly units of the elementary cell. A splitting of the glycine band is

Table 3. Band structure results of polydipeptides poly(gly-ala) and poly(gly-ser) in both α -helical and β -pleated sheet conformations. Symbols carry the same meaning as in table 1.

Poly	Band	$E_{\min}$	$E_{\max}$	ΔE	E_{gap}
<i>α-Helical conformation</i>					
Gly-ala	$n^* + 1$	3.065	3.391	0.326	14.887
	n^*	-11.874	-11.823	0.051	
Gly-ser	$n^* + 1$	2.683	2.919	0.236	14.541
	n^*	-11.898	-11.858	0.040	
<i>β-Pleated sheet conformation</i>					
Gly-ala	$n^* + 1$	3.697	3.967	0.270	15.769
	n^*	-12.147	-12.071	0.076	
Gly-ser	$n^* + 1$	4.022	4.171	0.149	15.344
	n^*	-11.329	-11.322	0.007	

observed because the first neighbour interactions are different for gly and gly' (ser-gly-gly' and gly-gly'-ser, respectively). The result is that the bands become even narrower than in poly(ser-gly) chains. The three bands located within the small energy range of 0.2 eV around 12.5 eV in the valence band region of poly(ser-gly-gly'gly'') chains (figure 2c) represent the three different glycine units. The central band, being broader than the other two bands, can be attributed to the gly' subunit because its both neighbours are glycine subunits. No change in the position of the states of ser subunits in the three poly(ser-*m*.gly) chains is observed because the neighbours of ser in all the three chains are glycine subunits. The splitting of the bands accompanied by a decrease in the band widths is expected from well-known general considerations.

The DOS curves for the conduction band region of periodic poly(ser-*m*.gly) chains are shown in figure 3. As is evident from figures 3a-c, the effect of increasing the number of glycine units in the elementary unit cell on the electronic structure and widths of the bands is similar to that observed in the case of the valence band region. Further, here too, the lowest unoccupied band in all the three chains corresponds to the ser unit and since its neighbours in all the three chains are glycine units, its position remains constant.

As in the case of homopolypeptides and polydipeptides, for poly(ser-*m*.gly) chains too, the fundamental energy gap is very large (~ 15.2 eV) and therefore these chains are expected to be insulating.

3.1c Periodic multicomponent polypeptides: In this section, the results of the electronic DOS of 3-, 4-, 5- and 6-component periodic polypeptide chains (in anti-parallel β -pleated sheet conformation) calculated (Bakhshi *et al* 1986a) on the basis of the *ab initio* matrix block NFC method are discussed. The six amino acid residues chosen for the study are glycine (gly), serine (ser), cysteine (cys), asparagine (asn), histidine (his) and aspartic acid (asp). Since the general features of the DOS curves of periodic multicomponent polypeptide chains are similar, we show here only a few DOS curves.

Figure 4 contains the electronic DOS curves for both the valence and conduction band regions of 6-component periodic polypeptide chains with the sequence (ser-gly-cys-asn-his-asp-). As is evident from this figure, both the valence and

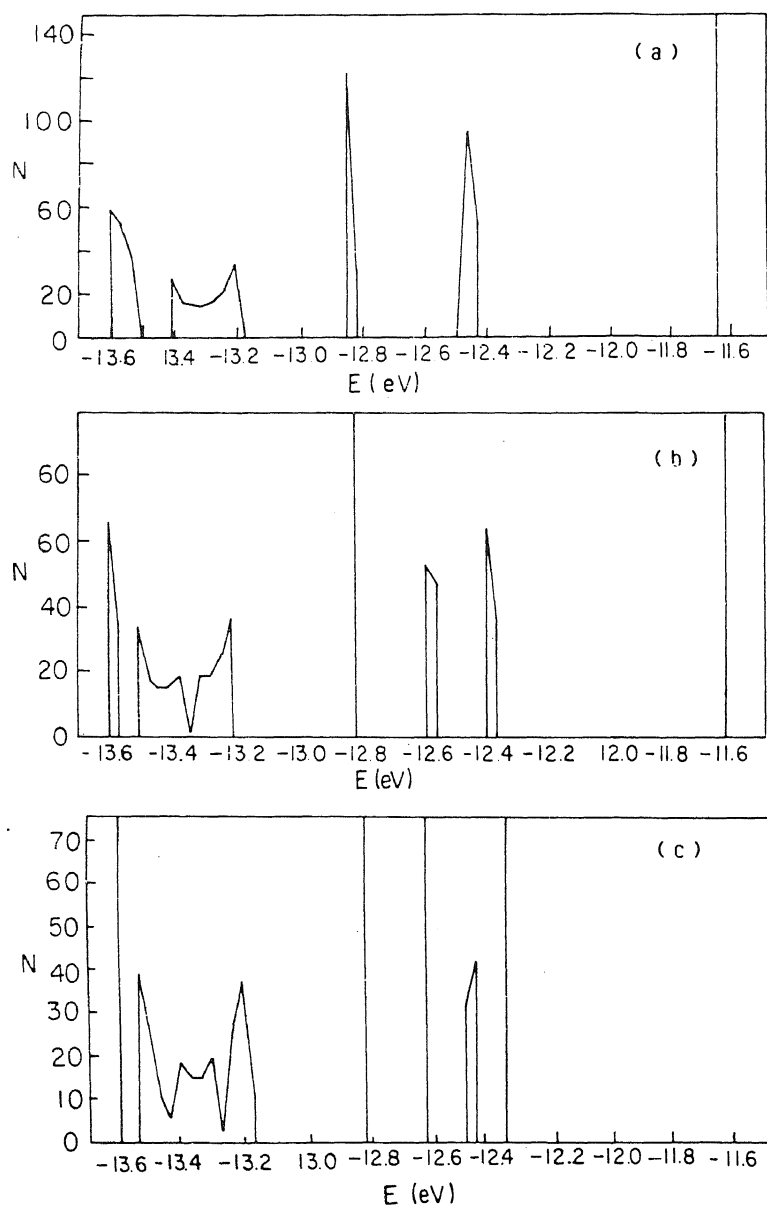


Figure 2. The density of states (DOS) of the valence band region of (a) poly(ser-gly), (b) poly(ser-gly-gly') and (c) poly(ser-gly-gly'-gly'').

conduction band regions of this chain consist of very narrow well-separated peaks – most of them being of equal intensity. The fundamental band gap for this chain is quite large (> 13.0 eV) and therefore this chain is expected to behave as insulating. Further since the peaks in the DOS curves are very narrow and well-separated, these chains are not likely to become conducting on doping with electron acceptors (p -doping) or with electron donors (n -doping) because neither

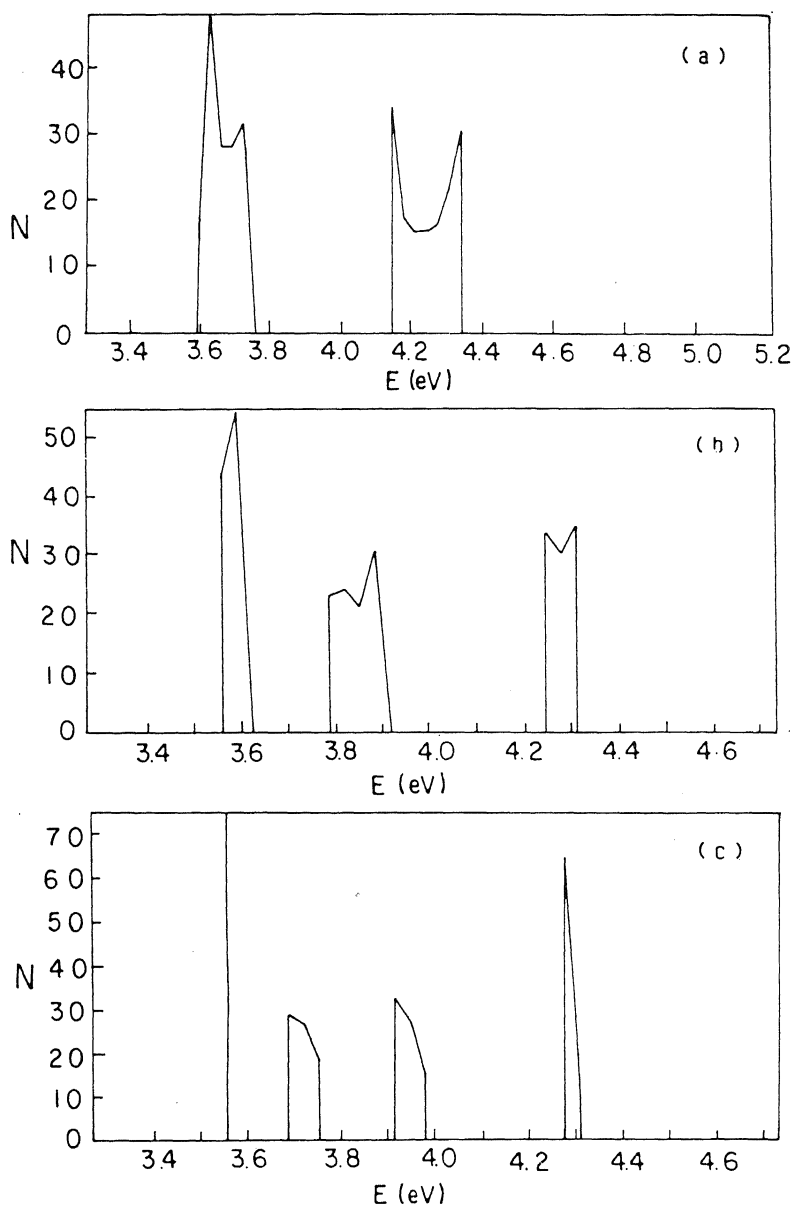


Figure 3. The DOS of the conduction band region of (a) poly(ser-gly), (b) poly(ser-gly-gly') and (c) poly(ser-gly-gly'-gly'').

band nor hopping conduction mechanisms are likely to become effective in these cases.

To see the dependence of the electronic DOS on the sequence of the amino acid residues in the periodic chain, the DOS curve for the valence band region of six component polypeptide chain with the sequence (ser-asn-asp-cys-gly-his) is shown in figure 5. Here too, the DOS curve consists of well-separated single peaks but in comparison to the earlier sequence the positions of the peaks are shifted. This shift

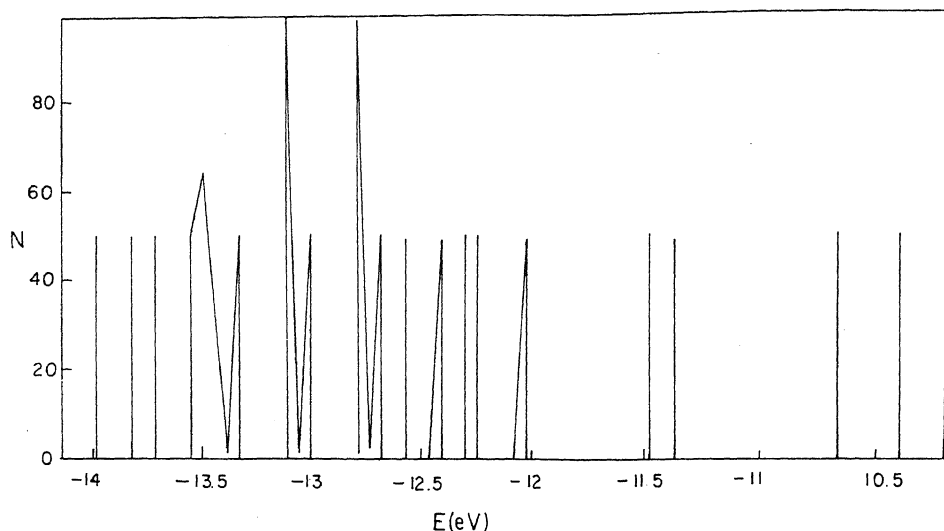


Figure 4. (a) The DOS of the valence band region of the periodic poly(ser-gly-cys-asn-his-asp).

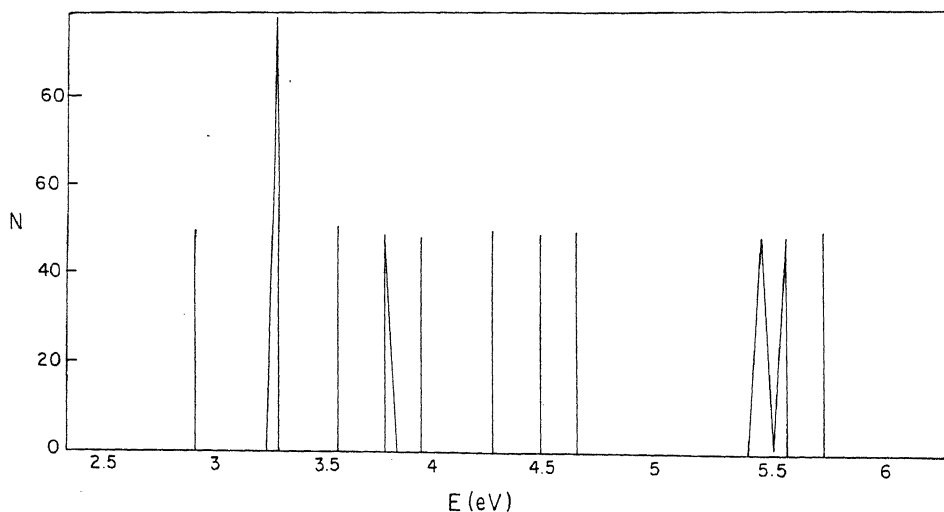


Figure 4. (b) The DOS of the conduction band region of periodic system in figure 4a.

in the positions of the peaks in the two sequences is due to the different first neighbour environments of the units in the two sequences.

3.2 Periodic DNA models

3.2a Nucleotide base stacks, poly base-pairs and polynucleotides: *Ab initio* Hartree-Fock CO calculations have been recently performed for single-stranded nucleotide base stacks (poly A, poly G, poly C and poly T), double-stranded poly base-pairs [poly(A-T) and poly(G-C)] and polynucleotides with adenylic acid (ASP) and thymidine (TSP) as repeating unit (Otto *et al* 1983). The computations

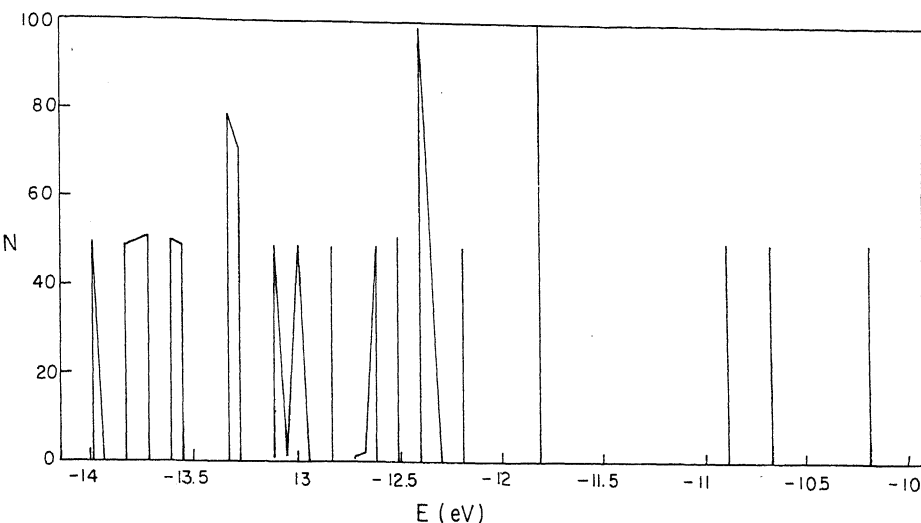


Figure 5. The DOS of the valence band region of periodic poly(ser-asn-asp-cys-gly-his).

have been performed using Clementi's (1977) minimal basis set and taking into account second neighbour interactions. The geometry of the molecules in the unit cell and the structural parameters of the helix have been obtained from the experimental data of DNA-B (Fieldman 1976). The coordinates for the hydrogen atoms have been added with the aid of a special computer program (Hermans *et al* 1976) making use of recently reported bond lengths and bond angles for the hydrogen atoms in the four bases (Clementi *et al* 1969) and in the sugar unit (Corongui and Clementi 1978). In the case of polynucleotides, for the electro-neutrality of chains a sodium ion has been attached to each phosphate group. The position of these added counter-ions was assumed to correspond to the one determined from quantum mechanical calculations on the interaction of one Na^+ ion and one sugar-phosphate fragment (Clementi 1980). This assumption, however, is only an approximation since the Na^+ ion in a chain of periodic polynucleotides interacts not only with one sugar-phosphate unit but also with the entire DNA chain (Clementi and Corongui 1981). For the largest studied DNA model, poly(ASP) with 125 basis functions, 42 h were needed to compute the two-electron integrals and 70 min for each iteration step on an IBM/370-3033 computer.

Table 4 contains the characteristics of the valence (n^*) and conduction ($n^* + 1$) bands of the four nucleotide base stacks while those of double-stranded poly base-pairs and periodic polynucleotides are given in table 5. In columns 3 and 4 are given the energy minima and energy maxima for each band while band widths are given in column 5. The energy of the corresponding molecular orbitals obtained on the basis of *ab initio* Hartree-Fock SCF LCAO MO calculations of the molecular system representing the unit cell are also given in the table. The fundamental energy gap value of each system is given in the last column of the table. The correspondence between the individual molecular levels and the bands is always unambiguous. Although the symmetry in the periodic chains is broken as a result of the stacked arrangement of the units, one can still define quasi π -type bands which are located mainly around the Fermi level.

Table 4. Band structure results of the four nucleotide base stacks. Molecular orbitals (MO) of the bases are also given for the sake of comparison. Symbols carry the same meaning as in table 1.

Poly	Band	$E_{\min}$	$E_{\max}$	ΔE	MO	E_{gap}
Cytosine (C)	n^*+1	1.697	2.517	0.820	1.638	10.434
	n^*	-9.526	-8.737	0.789	-9.945	
Thymine (T)	n^*+1	1.228	1.538	0.310	1.585	11.945
	n^*	-11.248	-10.717	0.531	-10.985	
Adenine (A)	n^*+1	2.184	2.444	0.260	1.924	12.121
	n^*	-10.117	-9.677	0.440	-10.369	
Guanine (G)	n^*+1	2.568	3.279	0.711	2.429	11.264
	n^*	-9.466	-8.696	0.770	-9.488	

Table 5. Band structure results of poly(G-C), poly(A-T), poly(ASP) and poly(TSP). Molecular orbitals (MO) of the base pairs are also given for the sake of comparison.

Symbols carry the same meaning as in Table 1.

Poly	Band	$E_{\min}$	$E_{\max}$	ΔE	MO	E_{gap}
A-T	n^*+1	1.716	2.011	0.295	1.536	11.712
	n^*	-10.516	-0.996	0.520	-10.137	
G-C	n^*+1	1.691	2.411	0.720	1.606	11.796
	n^*	-10.939	-10.099	0.840	-9.292	
ASP	n^*+1	2.646	2.926	0.280	—	12.160
	n^*	-9.824	-0.514	0.310		
TSP	n^*+1	1.989	2.309	0.320	—	11.788
	n^*	-10.099	-0.799	0.300		

It can be seen from table 4 that both valence and conduction bands for the four nucleotide bases are quite broad with their values ranging from 0.44–0.79 eV and 0.31–0.82 eV respectively. These band widths are much more than those obtained by the application of different semiempirical crystal orbital methods (Ladik 1971). Using the simple PPP-CO approximation (Ladik *et al* 1968; Ladik 1975) the corresponding values for the valence and the conduction bands are about 0.218 eV and 0.109 eV respectively. Energy band structure calculations for the base stacks on the basis of the CNDO/2 CO method (Suhai and Ladik 1973) give somewhat broader bands (valence band widths between 0.136–0.490 eV and conduction band widths 0.109–0.245 eV) whereas the MINDO/2 CO results (Ladik 1973; Suhai 1974) indicate somewhat less broad bands (widths of the valence band 0.027–0.299 eV and those of the conduction bands 0.027–0.163 eV).

Comparison of the results given in table 4 with the earlier *ab initio* band structure results using STO-3G minimal atomic basis set (Ladik and Suhai 1980) shows that the agreement between the two results is quite good. The positions of the valence and conduction bands and of the molecular orbitals are shifted by a constant value of 4.3 eV towards deeper energies due to the more flexible minimal atomic basis set used in these computations. Therefore both calculations predict a gap of more than

10 eV between the highest occupied and the lowest unoccupied bands in all cases. The large values of the band gap rule out the possibility of intrinsic conductivity in the four single-stranded base stacks.

In the case of the poly base-pairs poly(A-T) and poly(G-C) (see table 5), the positions and the widths of the bands can be related to those of the corresponding bases from which these pairs originate. In poly(A-T), the highest occupied (n^*) and the lowest unoccupied ($n^* + 1$) bands originate from poly(A) and poly(T), respectively, and therefore the first transition is of the inter-base type. In the case of poly(G-C) the results indicate again an inter-base type transition from G to C. Similar findings have been obtained with the aid of semiempirical PPP and CNDO/2 CO calculations (Avery *et al* 1969; Ladik 1973).

The widths of the valence and conduction bands for poly(ASP) and poly(TSP) (see table 5) have the same order of magnitude as the corresponding base stacks and poly base-pairs, indicating thereby that the possibility for Bloch-type conduction in these systems exists if free charge carriers (electrons or holes) are generated in them. In the pristine state, however, all these systems are expected to be insulating due to the large values of the fundamental energy gap (more than 10 eV) in them. Using the results for poly(ASP) and poly(TSP), it has been found, on the basis of Mulliken's population analysis, that the charge amounts of 0.212 and 0.190e per molecule pair are transferred from the sugar-phosphate chain to adenine and thymine respectively. This is in agreement with the results of a previous calculation for poly(ASP) (Ladik and Suhai 1980, in this computation in order to make the chain neutral, a hydrogen atom was attached to each phosphate group) in which a charge transfer of 0.187e from the sugar-phosphate unit to cytosine has been found. The internal electronic charge transfer in DNA-B has been the subject of recent computational investigations (Clementi and Corongui 1982). The different molecular fragments have been selected in such a way that each base is in a field similar to the one experienced in the biopolymer; the fragment consists of one phosphate group, two sugar residues and the base bound to one of the sugar units (SPS-base). In addition, to take into account the possible unit to unit charge transfer an even larger fragment of DNA-B has been studied, composed of three sugar units, two phosphate groups and two bases G and C. From these computations too, a charge transfer from the sugar units to the bases is obtained confirming the crystal orbital results. A quantitative comparison, however, shows a decrease of about 20% for poly(ASP) and poly(TSP) relative to the corresponding values obtained for the molecular models. The above difference may be due to the unit to unit interactions which are considered up to second neighbours in the periodic macromolecule. Another reason for the above discrepancy is that the interacting bases are different in the two computations. However it at least seems certain that a notable charge transfer from the sugar to the base occurs in DNA-B.

3.2b Single-stranded periodic multicomponent DNA base stacks: The electronic density of states of single-stranded periodic multicomponent (2, 3 and 4) DNA base stacks have been recently determined (Bakhshi *et al* 1986b) using the *ab initio* matrix block NFC method. The results for both valence and conduction band regions of 4-component periodic base stacks are shown in figure 6. As in the case of periodic multicomponent polypeptides, here too the DOS curves consist of very narrow well-separated peaks. The fundamental band gap in these periodic chains is

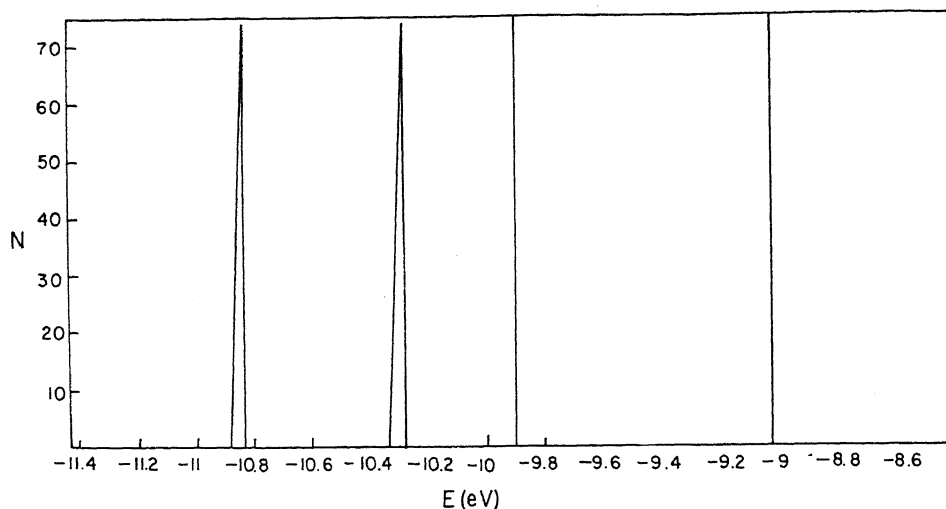


Figure 6. (a) The DOS of the valence band region of single-stranded periodic poly(AGCT).

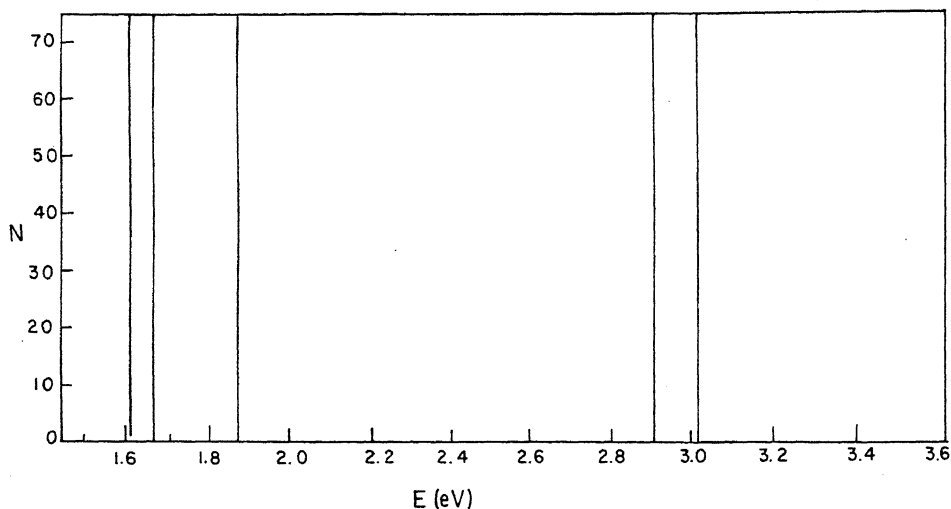


Figure 6. (b) The DOS of the conduction band region of the system in figure 6a.

also quite large and therefore there is no possibility of intrinsic conductivity in these chains. The reasons for the narrow peaks are the same as those given in §3.

4. Electronic structure of aperiodic protein and DNA models

4.1 Aperiodic protein models

4.1a Aperiodic multicomponent polypeptides: Aperiodic polypeptide chains are a more realistic model of proteins. The electronic DOS of 3-, 4-, 5-, and 6-component aperiodic polypeptide chains in the antiparallel β -pleated sheet conformation have

been recently determined on the basis of the *ab initio* matrix block NFC method (see §2.2b). There have been some studies in the past too, on the aperiodicity effects in proteins (Seel 1979; Suhai *et al* 1980) using a semiempirical method. The six amino acid residues chosen in the recent study are gly, ser, cys, asn, his and asp. Aspartic acid (asp) was considered in its neutral form. The various matrix blocks required for the study were obtained from the *ab initio* Hartree-Fock SCF LCAO study of 36 dimers which represent all possible combinations of two amino acid residues out of six. All the DOS calculations have been performed for a chain length of 300 units with an energy grid of 0.0002 a.u.

In figure 7 are shown the DOS distributions for both the valence and conduction band regions of aperiodic 6-component polypeptide chains in the composition (1:1:1:1:1:1). These DOS curves look strikingly different from the periodic polypeptide chain curves (figure 4). The sharp and well-separated peaks characterizing periodic chains are replaced by very broad regions of allowed energy states with a few small gaps in between. The broadening observed in the case of aperiodic polypeptides in contrast to periodic ones may be explained on the basis of fact that in the first neighbour interaction approximation the energy position of an amino acid residue in a sequence depends on the electronic environment of this residue. In the periodic case, the environment of each unit throughout the chain remains the same and therefore the peaks are very narrow. On the other hand, in an aperiodic chain, the electronic environment of a unit in the chain keeps on changing thereby shifting the energy position and thus leading to broadening of the region of allowed energy states (this broadening could also be explained on the basis of single and many environments, respectively, molecular exciton theory). Similar broadening has also been observed in the case of aperiodic DNA base stacks (Bakhshi *et al* 1986b), random copolymers of heterocyclic compounds (Bakhshi *et al* 1987c) and the random copolymers of acetylene with its nitrogen-containing analogues (Bakhshi and Ladik 1986), and with its mono- and difluoro derivatives (Bakhshi *et al* 1987a), respectively. As a result of this broadening, the fundamental energy gap in the case of aperiodic polypeptide chains is somewhat smaller than that of corresponding periodic polypeptide chains (because the valence bands move up and the conduction bands move down in energy), though its value is still too large for semiconduction to be possible at physiological temperature.

The effect of changing the sequence of units in an aperiodic chain has been investigated by determining the electronic DOS of a 300-unit long 6-component aperiodic peptide chain for a different sequence generated with the help of a Monte Carlo program. The resulting DOS curve for the valence band region is shown in figure 8. Comparison of the DOS curves for the two sequences (figures 7 and 8a) shows that the two curves, except for very small differences, are similar. It has been found that the average of three to five random chains can be considered to be converged and that averaging over more conformations does not change the picture any more. The reason why comparatively short chains of 300 units should be representative models, lies in the strong localizations of the electronic states. These localized states are relatively little affected by the chain length. The requirement that a chain length should meet is that the statistically possible different cluster arrangements should occur in the representative chain.

Finally the influence of changing composition of the components on the DOS

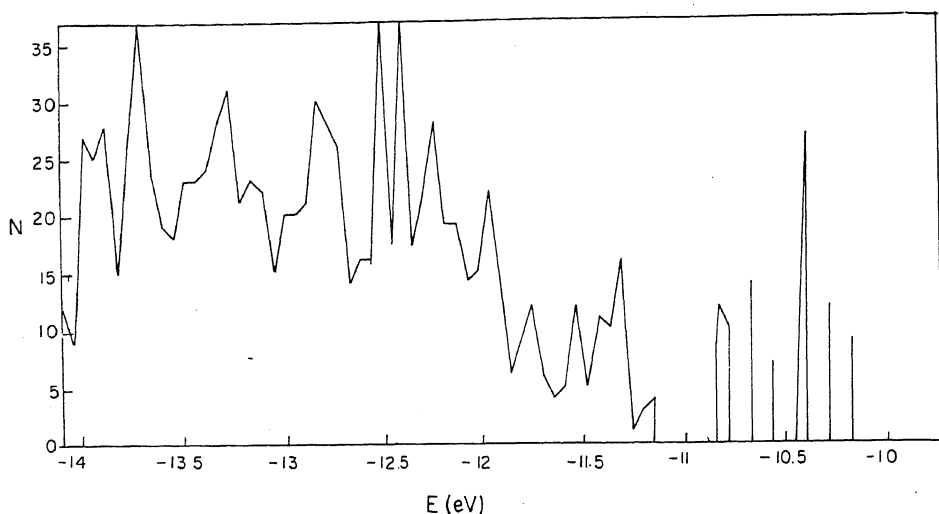


Figure 7. (a) The DOS of the valence band region of aperiodic poly(scr, gly, cys, asn, his, asp) (sequence I) in the composition (1:1:1:1:1:1).

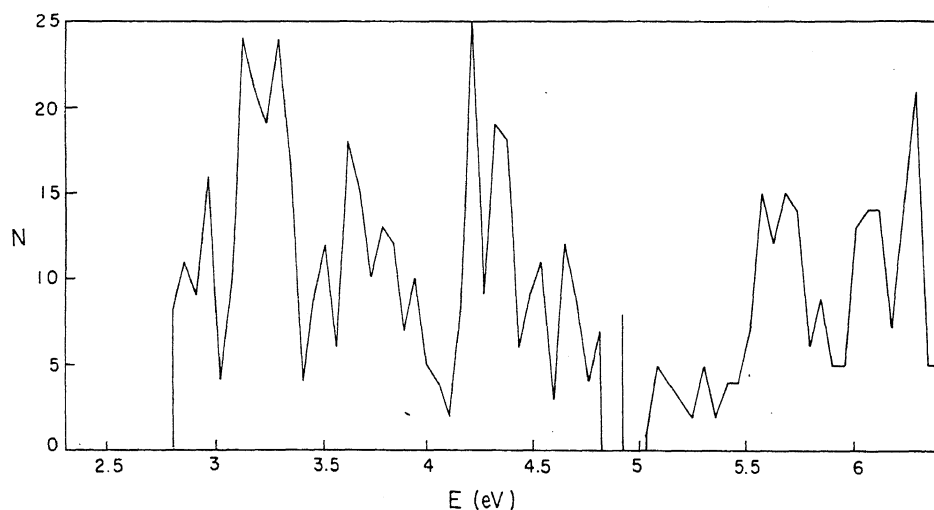


Figure 7. (b) The DOS of the conduction band region of the system in figure 7a.

curves is discussed. In figure 8b is shown the DOS curve of a 6-component aperiodic polypeptide chain with the composition of amino acid residues as ser – 5%, gly – 10%, cys – 15%, asn – 20%, his – 25% and asp – 25%. Comparison of this DOS curve with that with equal concentration of components (figure 7) shows that qualitatively both DOS curves look similar with the same regions of allowed and non-allowed energy states. The intensities of the allowed energy states in any region however are different due to the different concentrations of the components. These results illustrate that as long as concentrations do not change very much, the DOS distributions remain representative.

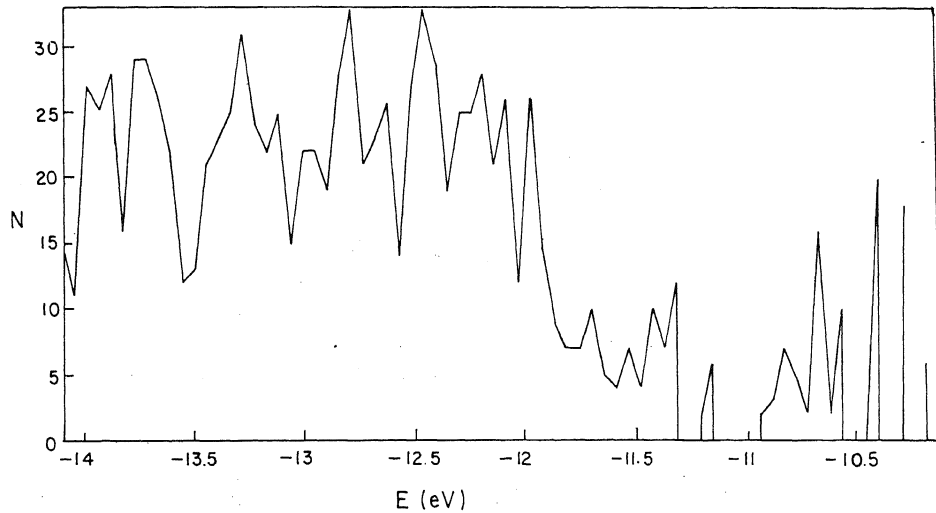


Figure 8. (a) The DOS of the valence band region of aperiodic poly(ser, gly, cys, asn, his, asp) (sequence II) in the composition (1:1:1:1:1:1).

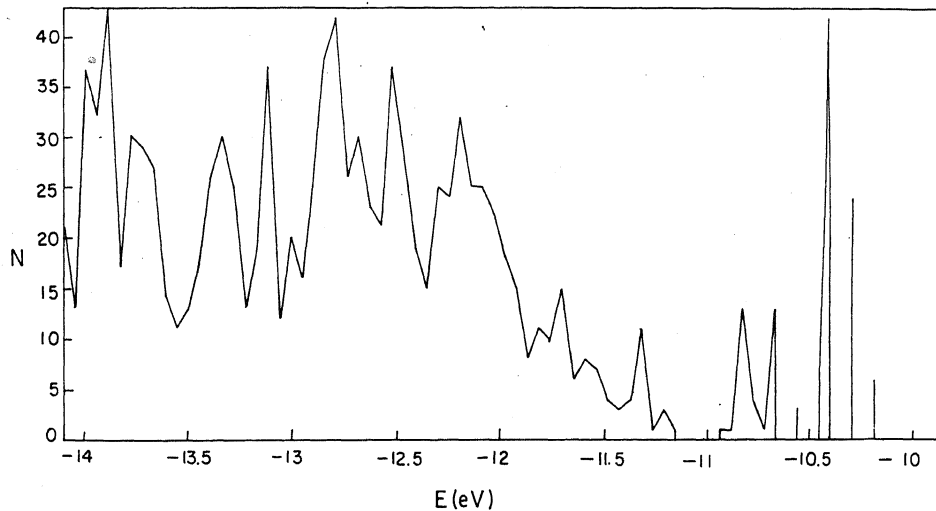


Figure 8. (b) The DOS of the valence band region of aperiodic poly(ser, gly, cys, asn, his) in the composition (1:2:3:4:5:5).

4.1b Conduction properties of aperiodic polypeptides: There is no possibility of intrinsic conductivity in periodic and aperiodic polypeptide chains due to their large fundamental energy gap. Since the bands in the DOS curves of aperiodic chains are very broad with a few small gaps, there is a possibility of extrinsic conduction [on doping with electron acceptors (*p*-doping) or with electron donors (*n*-doping)] in these chains. To decide about the nature of extrinsic conduction (whether coherent Bloch-type conduction or charge transport through hopping) one needs to investigate the localization properties of the wavefunctions belonging to the energy

levels in the upper part of the valence band region or the lower part of the conduction band region (these are the regions of interest if a charge transfer is to take place *in vivo* due to the interaction of proteins with electron acceptors or donors or with DNA).

The localization properties (Anderson localization, Anderson 1958, 1978) of the one-electron wavefunctions can be determined using the Inverse Iteration method (Wilkinson 1965). By applying this method in the case of the conduction band region of a 4-component aperiodic polypeptide chain (figure 9) the localization properties of the wavefunctions have been studied (Bakhshi *et al* 1986a) and the results of this study are given in table 6. Table 6 contains the first twenty-five states, the corresponding energies, the largest LCAO coefficient of the wavefunctions, the corresponding number of units (between 1 and 300) on which the wavefunction is localized, and the type of amino acid residue.

It is evident from table 6 that for the 4-component aperiodic polypeptide chain, the one-electron wavefunctions are highly localized thereby making the charge transport through hopping between these states rather probable. Similar results have been obtained by us recently in the case of a 6-component aperiodic polypeptide chain (Bakhshi *et al* 1987b) and therefore we do not show them here. If we assume a 0.1e charge transfer per unit to the chain, the Fermi level for the 4-component chain lies at 3.06391 eV (eigenvalue number 15 in table 6). Considering first excitations from these fifteen occupied states to the next ten empty ones, one first neighbour pair (193-192) is in this group, namely the excitation from level 12 to 23. If higher excitations are also considered or the fact that some of the occupied levels become empty due to excitations is taken into account, the following excitations between first neighbours can be found (the number of the participating unit cells are given in parentheses): excitations from level 7 to 9 (192, 193), from 8 to 9 (192, 193) from 27 to 31 and 32 (98, 97), from 16 to 51 (149, 150), from 12 to 37 (193, 194), from 37 to 44 and 45 (194, 193). Possible excitations between second neighbour pairs are excitations from level 13 to 17 (249,

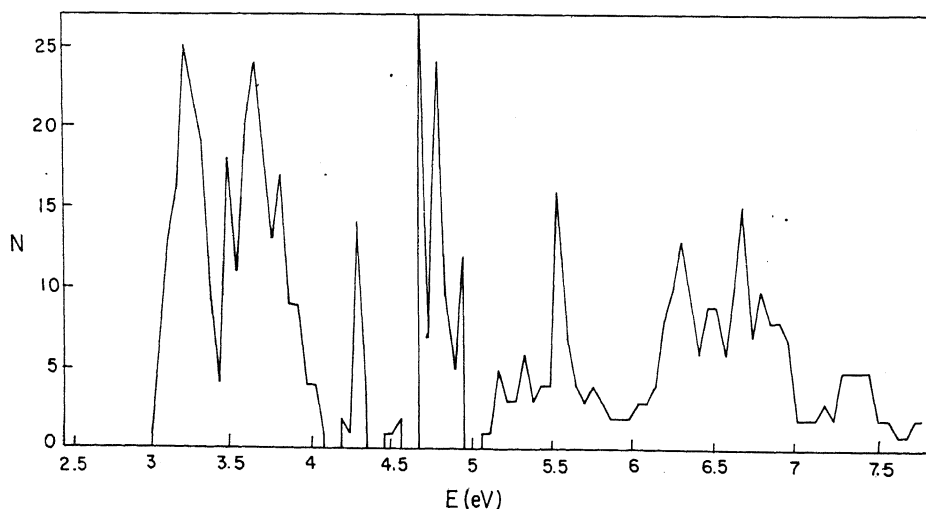


Figure 9. The DOS of the conduction band region of aperiodic poly(ser, gly, cys, asn).

Table 6. Orbital energy E_i , the largest LCAO coefficient C_{imax} of the one-electron wavefunction, the corresponding number of the unit N_{unit} (between 1 and 300) on which the wavefunction is localized and the type of the unit for the lowest 25 unoccupied states of aperiodic poly(gly,ser,cys,asn) chain whose DOS distribution is shown in figure 9.

i	E_i (eV)	C_{imax}	N_{unit}	Type
1	2.98441	0.939	252	ser
2	2.99009	0.755	207	asn
3	2.99557	0.687	101	asn
4	3.00145	0.797	63	ser
5	3.00713	0.871	63	ser
6	3.01280	0.902	24	ser
7	3.01848	0.693	192	gly
8	3.02416	0.890	192	gly
9	3.02984	0.802	193	gly
10	3.03552	0.873	108	gly
11	3.04119	0.792	227	asn
12	3.04688	0.896	193	gly
13	3.05255	0.893	249	ser
14	3.05823	0.775	210	ser
15	3.06391	1.230	81	asn
16	3.06959	0.762	149	gly
17	3.07527	0.647	251	asn
18	3.08085	0.901	108	gly
19	3.08662	0.708	63	ser
20	3.09231	0.902	108	gly
21	3.09799	0.901	108	gly
22	3.10366	0.749	134	asn
23	3.10934	0.795	192	gly
24	3.11502	0.904	192	gly
25	3.12070	0.905	192	gly

251) and from 26 to 37 (192, 194). There are also some possible excitations within the same unit. These excitations can help to promote an electron to a higher level from which it can be excited in a subsequent step to an orbital which is localized on a different site.

In order to explore the possibility of hopping conduction in aperiodic polypeptides, one needs to determine the primary jump rates for the electrons to hop between localized states with energies near the Fermi energy. The primary jump rate $P_{i \rightarrow j}$, that is, the number of jumps from one localized state i to another site j is given to a good approximation (Mott and Davis 1971; Grunewald *et al* 1984; Grunewald *et al* 1985) by

$$P_{i \rightarrow j} = \nu_{\text{phonon}} [\exp(-\alpha |R_i - R_j|)]^2 \exp(-\Delta E_{ij}/kT), \quad (26)$$

where $\Delta E_{ij} = E_j - E_i$, R_i and E_i are the position and energy of the electron localized at site i , $\exp(-\alpha |R_i - R_j|)$ is the overlap integral between two exponentially localized wavefunctions (Ziman 1979). If the LCAO expression is used for this overlap integral and approximated by the dominant terms, then one obtains

$$P_{A \rightarrow B} = \nu_{\text{phonon}} \left(\sum_r \sum_s c_{ir} c_{js} \langle \chi_r | \chi_s \rangle \right)^2 \exp(-\Delta E_{ij}/kT). \quad (27)$$

Here C_{ir} and C_{js} are the dominant LCAO coefficients of the wavefunctions ψ_i (ψ_j) which are localized at site A (B) and belong to the energies E_i and E_j , respectively.

Using the data given in table 6 and taking the phonon frequency ν_{phonon} for proteins to be 10^{12} s^{-1} corresponding to the most acoustical modes, the primary jump rates have been calculated from (27). These results are shown in table 7. The first two values refer to hopping between first neighbours and are 5×10^7 and $7 \times 10^8 \text{ s}^{-1}$, respectively. As the characteristic value for second neighbour hopping 10^5 jumps per second are obtained. The last three entries give primary jump rates between orbitals localized in the same unit cell. The primary jump rates for these local excitations are between 7×10^{11} and $9 \times 10^{11} \text{ s}^{-1}$ – the small differences are due to differences in the overlap between the initial and final states. It can be shown that if a more realistic estimate of average excitation energy is taken into consideration (Bakhshi *et al* 1986a) then the Boltzmann factor decreases by about 10^{-1} and therefore the physically most interesting first and third $P_{A \rightarrow B}$ values in the table have to be decreased by this value. Comparison of these primary jump rates for proteins calculated using *ab initio* one-electron wavefunctions with the ones obtained for other non-crystalline solids (Mott and Davis 1971; Silver *et al* 1982) shows that the agreement between the two values is quite good.

The above results in the case of aperiodic polypeptide chains strengthen the possibility of the validity of Szent Gyorgyi's 45-year old prediction (Szent Gyorgyi 1941) that the various biological phenomena could be explained on the basis of fact that proteins become conductors of electricity instead of insulators under certain circumstances. Szent Gyorgyi (1957, 1960, 1968, 1976) also gave a theory according to which there is a close relationship between conduction in proteins and cancer. According to him easy transport of charge and energy is necessary for the normal functioning of the cell and that if this flow of charge and energy is hindered it can lead to a cancerous state. To verify the predicted hopping conduction in proteins, one needs to prepare, using a combination of molecular biological (cloning) and synthetic methods, very pure and characterised samples of polypeptides with

Table 7. Characteristic primary jump rates P_{A-B} (in s^{-1}) calculated from (27) for the aperiodic poly(gly,ser,cys,asn) chain (corresponding to its DOS distribution given in figure 9). A, B , denote the localization sites, i, j the corresponding number of energy levels. ΔE_{ij} (in eV) the energy difference entering the Boltzmann factor ν_{phonon} was chosen to be 10^{12} s^{-1} $KT = 2.67 \times 10^{-2} \text{ eV}$ for $T = 310 \text{ K}$.

A	B	i	j	ΔE_{ij}	P_{A-B}
193	192	12	23	0.062	5×10^7
192	193	8	9	0.006	7×10^8
192	194	26	37	0.062	1×10^5
192	192	7	8	0.006	7×10^{11}
108	108	18	20	0.011	7×10^{11}
108	108	20	21	0.006	9×10^{11}

different known sequences and possibly more or less homogeneous lengths (Ladik *et al* 1986). Only after preparing such well-defined samples (the preparation of which actually needs the development of the material science of biopolymers) is it worthwhile to try to dope them. Due to the polyelectrolytic nature of these chains, doping with the usual inorganic dopants will not work and so one has to use a combination of doping with organic dopants and electrochemical doping. After having successfully doped the well-defined samples of polypeptides, one can perform on them measurements of transport properties using high frequency alternating currents (otherwise instead of measuring intrinsic hopping conductivity and other transport properties in these polycrystalline materials, one would end up by determining the contact potentials between the electrodes and the samples and the potential barriers between the different chains). By changing systematically the sequences of these polypeptide samples one can study the effect of sequence changes on charge (and also energy) transport in these biopolymers.

4.2 Aperiodic DNA models

4.2a Single stranded aperiodic DNA and a fragment of human gene: Different DNA molecules differ in the sequence of the four nucleotide bases A, T, G and C in a strand, though the two right-handed antiparallel sugar-phosphate strands of a DNA molecule are held together by the base pairs A-T and G-C. The major difficulty in the investigation of the electronic structure of DNA lies in the treatment of the non-periodic arrangement of the bases. Since it is not possible to perform direct SCF calculations, one has to employ approximate methods. The first step in the treatment of aperiodicity in DNA from a solid state physical point of view was made by Day and Ladik (1982) who used the cluster coherent potential approximation (CCPA) in the Huckel level to obtain the DOS in a double helix with a random base pair sequence.

Recently the electronic DOS of single-stranded aperiodic DNA base stacks in the biologically important B-conformation have been determined (Bakhshi *et al* 1986b) using the *ab initio* matrix block NFC technique. The DOS of the valence band and conduction band regions of 300-unit long single-stranded aperiodic poly(AGCT) in the composition (1 : 1 : 1 : 1) are shown in figure 10. As in the case of aperiodic polypeptide chains, here too, the DOS curves consist of much broader peaks though the regions still have many gaps. As a result of this broadening, the fundamental energy gap decreases to a value of 10-30 eV in the aperiodic case. The reasons for this broadening have already been discussed in §4.

To see the dependence of the DOS on the sequence of units producing it, both valence and conduction band regions of aperiodic poly(AGCT) have been studied with different random sequences of 300 units generated with the help of the Monte Carlo program. As an illustrative example, figure 11 shows the DOS of the valence band region for a sequence (II) different from the one used in the figure (sequence I). Comparing the DOS for sequences I and II, one notices differences both near the upper limit of the valence band regions and in the other parts of the spectrum of the valence band regions. Similarly other individual DOS curves were found to be slightly different. However the average curves of three and four sequences, respectively, were nearly completely identical and so one can take them as a good approximation to the DOS of an ensemble-averaged random sequence.

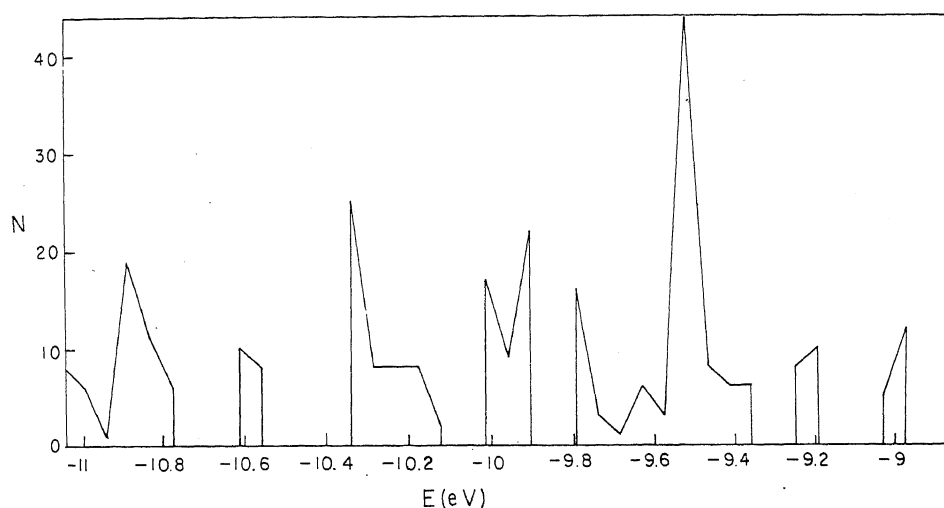


Figure 10. (a) The DOS of the valence band region of single-stranded aperiodic poly(AGCT) (sequence I).

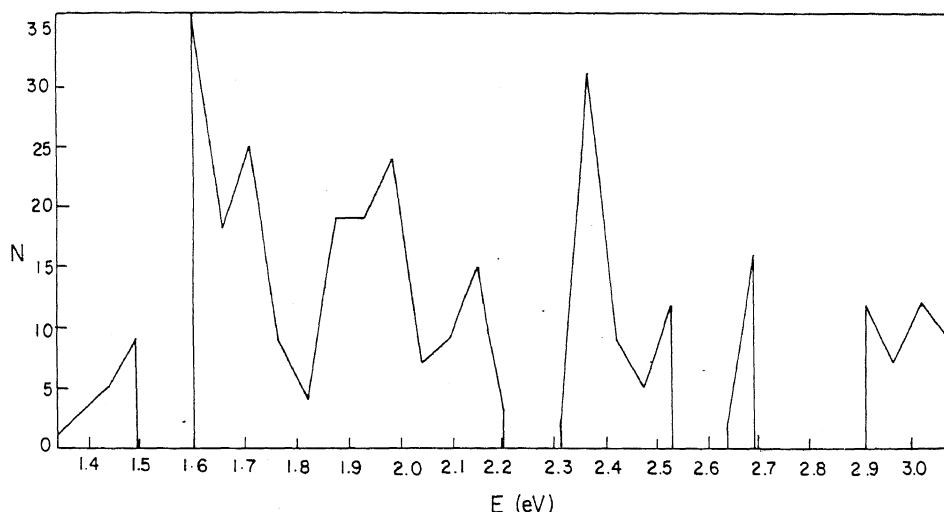


Figure 10. (b) The DOS of the conduction band region of the system in figure 10a.

Following recent advances in biochemistry it has become possible to establish an extensive nucleotide base sequence bank of a large number of genes. Certain sequences of nucleotides from oncogenes are known to be responsible for the initiation of some forms of cancer. The electronic DOS of one such gene of the Alu family isolated from fetal liver DNA (Gentleman *et al* 1984) has been recently determined for the first time (Bakhshi *et al* 1986b). This fragment has a chain length of 825 nucleotide bases and starts about 6000 residues after the end of the proinsulin gene. The DOS curves of the valence band and the conduction band regions of this gene show a great deal of similarity to the corresponding DOS curves of aperiodic poly(AGCT) and therefore we do not show them here.

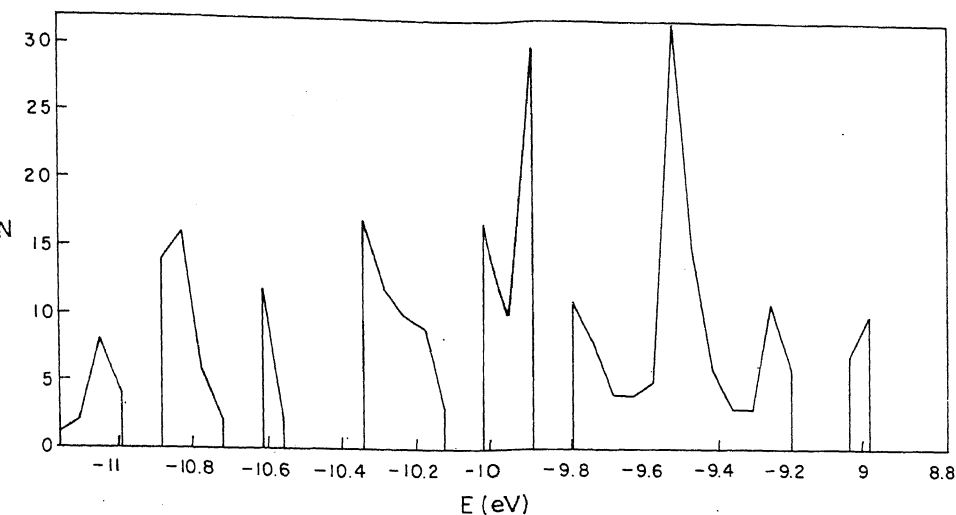


Figure 11. The DOS of the valence band region of single-stranded aperiodic poly(AGCT) (sequence II).

4.2b Conduction properties of aperiodic DNA: The fundamental energy gap in the case of aperiodic DNA, as in the case of aperiodic polypeptide chains, is very large and therefore there is no possibility of intrinsic conduction in aperiodic DNA. As regards the possibility of hopping conduction, nothing definite can be said because the gaps in the DOS curves of aperiodic poly(AGCT) are too numerous and large to allow an effective charge transport by hopping even if free charge carriers (probably due to charge transfer) are present. It needs to be mentioned here that in the present study only the interactions between the nucleotide bases in the direction of the helix are considered. In real DNA, on the other hand, there are two antiparallel strands of nucleotide bases in the inner part of the double helix. It is, therefore, quite likely that because of these additional interactions between the bases, the structure of the DOS curves gets further modified leading to some further broadening of the peaks. Only then one can investigate the possibility of hopping conduction in DNA, as has been done in the case of aperiodic polypeptide chains. Experimentally, in the case of DNA also one needs to prepare very pure and well-defined samples of polynucleotides in order to carry out more accurate and more reliable physical measurements on them.

5. Treatment of correlation in biopolymers

5.1 Periodic polymers

One of the principal deficiencies of the Hartree-Fock crystal orbital method is the neglect of the correlation between motions of electrons with opposite spins. Conduction band electrons and valence band holes are regarded as "bare" particles moving in the average periodic self-consistent potential produced by the nuclei and the other electrons that do not respond to the presence of extra particle. The result is that the Hartree-Fock method overestimates the fundamental energy gap. The treatment of correlation in polymers is necessary not only for a more exact

determination of their electronic properties but also for the determination of electronic structure in non-equilibrium geometry and in an excited state. The methods used in the treatment of electron correlation fall into two categories. The configuration interaction (CI) method which is not size-consistent (i.e. in a given level of approximation gives less and less correlation energy per electron if the number of electrons increases and in the limit $E_{\text{corr}}/n \rightarrow 0$ if $n \rightarrow \infty$, where n is the number of electrons) and methods like the many-body perturbation theory (Moeller and Plesset 1934; Paldus and Cizek 1975, Kapuy *et al* 1983; Pople *et al* 1983) and the coupled cluster theory (Cizek 1966, 1969; Cizek and Paldus 1971; Paldus and Cizek 1975) which are size-consistent can therefore be used for the calculation of correlation in polymers. Two approaches are used while calculating correlation in the polymers. In the case of insulators or semiconductors with a noncrossing completely filled valence band and an empty conduction band one can always use localized Wannier functions instead of the delocalized Bloch functions. This procedure is not possible in the case of metals because no Wannier functions can be constructed from the Bloch states belonging only to the filled part of the valence band. In such cases one has to use other methods. Using the size-consistent methods electron correlation has been considered in the calculations for an H chain (Suhai and Ladik 1982), polyacetylene (Suhai 1983a), polyethylene (Suhai 1983b), and recently for a cytosine stack (Suhai 1984).

If the Moeller-Plesset perturbation theory is used in second order (MP/2), (Ahlrichs and Kutzelnigg 1968; Meyer 1973) it can be shown that the total second-order perturbation contribution can be easily partitioned into a double sum of pair correlation energies

$$E_2 = \sum_{I,J} \varepsilon_{I,J}, \quad (28)$$

where

$$\varepsilon_{I,J} = \sum_{A,B} \frac{|\langle \phi_I(1) \phi_J(2) | \frac{1}{r_{12}} (1 - P_{12}) | \phi_A(1) \phi_B(2) \rangle|^2}{\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B} \quad (29)$$

Here the combined indices I, J stand for filled Bloch orbitals ϕ_I, ϕ_J etc. and they indicate both a band index i and k value k_i . In the same way ϕ_A and ϕ_B stand for unfilled Bloch orbitals. P_{12} is the exchange operator.

Using the definitions (28) and (29) and also applying Koopmans theorem, one can easily show that HF conduction and valence bands can be corrected for correlation and that one obtains a quasiparticle (QP) band structure (Suhai 1983a) in the form

$$\varepsilon_C(\text{QP}) = \varepsilon_C(\text{HF}) + \sum_C^{(N+1)} (e) + \sum_C^{(N+1)} (h), \quad (30)$$

$$\varepsilon_V(\text{QP}) = \varepsilon_V(\text{HF}) + \sum_V^{(N)} (e) + \sum_V^{(N)} (h), \quad (31)$$

where $\Sigma(e)$ and $\Sigma(h)$ are the electron and hole self-energies which arise if one puts an extra electron into the conduction band (the composite index C indicates this) or creates a hole in the valence band (denoted by index V), and can be expressed as changes in the sum (28) of pair correlation energies resulting from these processes (Suhai 1983a). These corrections have been shown to lead to a decrease in the band gap and in the band widths.

The quasiparticle band structure calculations using the second-order Moeller-Plesset perturbation theory have been recently performed (Suhai 1984) for a cytosine stack. The superimposed nucleotide bases were kept in the same relative position as in DNA-B. The calculations were performed using the 4-31G basis set (Ditchfield *et al* 1971). The results of the calculations are shown in table 8. It can be seen from table 8 that the self-energies shift the conduction band to the lower energies and the valence band to higher energies. It is also observed that the shift is somewhat larger at the top than at the bottom of the conduction band leading to an effective band narrowing. At the same time, the terms produce a stronger shift at the bottom of the valence band than at its top (this situation is analogous to the Franck-Condon effect in phonon theory). The HF conduction band is shifted in this way by ~ 1.2 eV downwards and the valence band by ~ 1.3 eV upwards, thereby reducing the fundamental gap from ~ 10.5 eV to ~ 8 eV.

It is thus seen that by using a medium level basis the correlation to the gap is rather large (~ 2.5 eV) (much larger than the ~ 1.45 eV value in the case of polyacetylene with the 6-31G** basis set). This is most probably due to the fact that a cytosine molecule (with 8 non-H atoms) is much larger than a C_2H_2 unit (only 2 non-H atoms). Therefore one would expect that by using the same refined basis (due to both basis set effects and 70–75% of the correlation) one would obtain a gap between 6.0 and 7.0 eV. If one extrapolates this gap again to 100% correlation one would end up most probably with a gap of ~ 6.0 eV. This value is not far from the values of 5.0–5.5 eV which one expects from the exciton spectra of the nucleotide base stacks, namely the lower edge of the first singlet exciton band, which lies at ~ 4.3 eV and has a width of 0.6 eV (Tinoco 1960; Devoe and Tinoco 1962).

Table 8. Single particle energies ϵ (HF) and self-energy correlations (Σ) contributing to the quasi-particle energies in the valence and conduction bands of poly(C). Results obtained using 4-31G basis set and second order Moeller-Plesset/2 perturbation theory. (All quantities are in eV).

	Valence band	Conduction band	gap
$\epsilon_{\max.}$ (HF)	-8.203	3.084	10.499
$\epsilon_{\min.}$ (HF)	-9.039	2.296	
$\Sigma(e)$ at band max.	-0.574	-1.470	
$\Sigma(e)$ at band min.	-0.631	-1.461	
$\Sigma(h)$ at band max.	1.846	0.203	
$\Sigma(h)$ at band min.	2.007	0.254	
$\epsilon_{\max.}$ (el. pol.)	-6.931	1.817	
$\epsilon_{\min.}$ (el. pol.)	-7.663	1.089	8.020

5.2 Aperiodic polymers

The treatment of correlation effects in aperiodic polymers is still largely an unresolved problem. The knowledge of the correlated electronic density of states on the other hand, is highly desirable for a better understanding of the electronic structure of aperiodic proteins and DNA. To consider the correlation effects in nonperiodic polypeptides and DNA base stacks, one can pursue two kinds of strategies. One can perform *ab initio* band structure calculations for all the four base stacks in the case of DNA-B using a good basis set (double ζ + polarisation functions) and then compute from them the quasi-particle band structures using the Moeller-Plesset (MP) (1934) many-body perturbation theory in second-order (MP/2) to obtain the major part of the electron correlation effects. Having obtained the quasi-particle band structure results for all the 4 base stacks and 20 homopolypeptides, one can use them to fit the Huckel parameters α_i and $\beta_{i-1,i}$ (see §2.2a) necessary for a simple (one band) NFC calculation of the DOS of a single-stranded aperiodic DNA base stack or aperiodic polypeptide chain. One has to fit the α_i and $\beta_{i-1,i}$ parameters for the valence and conduction band regions from the quasi-particle valence and conduction bands of the corresponding periodic chains. In this way one could treat the physically interesting energy regions of any native protein or DNA with known sequences by applying a good basis set and taking into account the major part of electron correlation.

The other strategy is to consider correlation effects using the *ab initio* matrix block NFC method. First of all one can determine the electronic DOS for single-stranded aperiodic DNA base stacks (and for 6–7 component aperiodic model protein) using the *ab initio* matrix block NFC technique with better basis sets. One can then investigate the localization properties of one-electron wavefunctions belonging to each energy level of both the valence and conduction band regions of each chain using the inverse iteration technique. Finding out in this way on which amino acid (base) a given wavefunction is localized, one can find out the quasi-particle (correlated) band structure of the corresponding homopolypeptide (base stack). As compared to the uncorrelated HF bands, the quasi-particle bands are shifted (the conduction bands downwards and the valence band upwards) thus decreasing the gap. Taking this shift at the centre of the band under consideration one can shift the investigated energy level in the DOS distribution by the same amount. Doing this procedure for every level of the aperiodic polypeptide chain (base stacks), (which would mean different shifts for levels with wavefunctions localized on different types of amino acid residues (bases) one would obtain an approximate correction of the DOS curve due to correlation effects.

Acknowledgements

I would like to express my gratitude to all the people who contributed to this work. I am deeply indebted to all my colleagues in Erlangen, in particular to Prof. J Ladik who introduced me to polymer quantum chemistry and to Prof. P Otto and Dr. M Seel for their enthusiastic collaboration. My special thanks are to the "Deutsche Akademischen Austauschdienst (DAAD)" for the award of a fellowship and to the University of Delhi for leave. I am also indebted to Prof. E Clementi (IBM Company, Kingston) for his interest and support for this work and to the IBM

Kingston, IBM Italy, IBM Germany, and Kraftwerk Union AG, for providing us with free computer time. The financial support of the National Foundation for Cancer Research (NFCR), USA and the "Fond der Chemischen Industries", West Germany, is also gratefully acknowledged.

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Binding of 1-anilinonaphthalene-8-sulphonate to poly(N-vinyl-2-pyrrolidone)

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MS received 29 August 1987

Abstract. The binding of 1-anilinonaphthalene-8-sulphonate (ANS) to poly(N-vinyl-2-pyrrolidone) (PVP) of molecular weight grades k30 (molecular weight 40,000) and k90 (360,000) was studied by a dialysis technique in 0.05 M phosphate buffer, pH 7.1, at different temperatures. The intrinsic binding constant, K , was determined. The binding was favoured by negative enthalpy and positive entropy in both the systems indicating respectively that energetic forces and hydrophobic interactions were contributing to the binding affinity. The effects of addition of urea and palmitic acid on binding were investigated by dialysis and fluorescence techniques. The results showed that the binding of ANS to PVP was dependent on the nature and microenvironment of the binding sites and thereby pointed out the importance of the iceberg structure of water in the binding system.

Keywords. Binding; 1-anilinonaphthalene-8-sulphonate; poly(N-vinyl-2-pyrrolidone); dialysis; fluorescence.

1. Introduction

Poly(N-vinyl-2-pyrrolidone) (PVP) is a water-soluble synthetic polymer. It resembles the biopolymer bovine serum albumin in many respects, such as presence of amide linkage and preferential binding to anionic substrates. Owing to its excellent properties, PVP finds applications in many fields like the pharmaceutical industry, blood plasma substitutes, cosmetics and textiles. Because of its resemblance to biopolymers, the study of binding of ligands to PVP helps in understanding the functions of proteins and enzymes in physiological systems.

Ligands with a variety of structures, viz., dyestuffs (Frank *et al* 1957; Maruthamuthu and Sobhana 1979; Maruthamuthu and Dhandavel 1980; Maruthamuthu and Subramanian 1985), aromatic compounds (Molyneux and Frank 1961), drugs (Horn and Ditter 1982) and simple ions like fluoride (Maruthamuthu and Reddy 1984) have been reported to bind to PVP. In the present work we report the results of our study of the binding of 1-anilinonaphthalene-8-sulphonate (ANS), a hydrophobic and fluorescent probe, to PVP. Hydrophobic fluorescent probes are

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very useful (McClure and Edelman 1966) for locating hydrophobic binding sites in proteins and synthetic polymers; changes in fluorescence properties upon binding indicate conformational changes and binding site microenvironments of the macromolecules. An NMR study of the mechanism of ANS binding to PVP has already been reported (Kono *et al* 1973). Nevertheless a detailed study of the nature of binding, interacting forces and the effect of structuring of solvent medium on binding sites has not yet been made. Therefore the present study was attempted to investigate these factors to understand more about the ANS-PVP system.

2. Experimental

PVP of two molecular weight grades k30 and k90 (approximate molecular weights 40,000 and 360,000, respectively) was used. k30 PVP was obtained from Loba Chemie, India, and k90 from Sigma Chemical Company, St. Louis, USA. Water content of polymer samples was determined by drying a known quantity in an air-oven at 110°C for 2 days, and was found to be 13% and 6% for k30 and k90, respectively. Correction for this was made in expressing PVP concentrations. ANS was purchased as the free acid from Sigma, USA. Other chemicals used, viz., buffer reagents, urea and palmitic acid, were of reagent grade. All the chemicals were used without further purification.

All the experiments – dialysis, fluorescence and viscosity – were carried out in 0.05 M KH_2PO_4 - Na_2HPO_4 buffer, pH 7.1.

The procedure for the dialysis experiment has been described elsewhere (Alexander and Block 1961). A concentration of 2.25×10^{-2} M in terms of monomer units was chosen for both the PVP samples. 10 ml polymer solution taken inside a semipermeable cellophane bag (Sigma, USA) was allowed to equilibrate against 10 ml ANS solution (in the concentration range 10–80 μM) for one day. A preliminary experiment showed that 16 h was the equilibration time and that binding of ANS to the cellophane bag was negligible. The free ANS concentration was determined by measuring absorption at 266 nm in a Carl-Zeiss UV-VIS spectrophotometer. The dialysis experiment was carried out at 3, 25 and 40°C.

The fluorescence emission of ANS was investigated at room temperature using an Aminco-Bowman spectrophotofluorimeter. The effect of urea and palmitic acid on binding was studied both in the fluorescence and dialysis experiments.

Viscosities of k30 PVP solution in buffer alone and in the presence of ANS were measured with an Ubbelohde suspended level viscometer at 30°C. The viscometer had a flow time of 134 s for double-distilled water and 137 s for buffer solution, which allowed us to neglect kinetic energy correction.

Linear regression analysis was used to calculate the binding parameters.

3. Results and discussion

The ANS-PVP system was analysed in terms of a simple model of binding. According to this, ligand molecules bind to linear independent binding sites on the

polymer. Based on this model, Klotz (Alexander and Block 1961) has proposed the following equation.

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nKc}, \quad (1)$$

where r = number of moles of ligand bound per mole of monomer units of polymer, n = number of binding sites per mole of monomer units, $1/n$ = number of monomer units required to constitute one binding site, K = intrinsic binding constant and c = equilibrium or free ligand concentration. As required by (1), in a plot of $1/r$ vs. $1/c$, a straight line was obtained in each dialysis experiment (figure 1), proving that the above simple model of binding holds good in the ANS-PVP case also. From the slope and intercept, the binding parameters $1/n$, nK , the first binding constant, and K were calculated and are given in table 1. Since the experiment was made at different temperatures, thermodynamic parameters have been calculated using the temperature coefficient of K and presented in table 2.

The effect of urea and palmitic acid on the binding of ANS to PVP was studied using k30 PVP. The effect is illustrated in table 3 by the changes in r values. In dialysis experiments performed to study the effect of addition of these compounds, a lower PVP concentration ($3.6 \times 10^{-3} \text{M}$) was used, whereas in the dialysis experiments earlier described a PVP concentration of $2.25 \times 10^{-2} \text{M}$ was maintained. The reason for this has been described later.

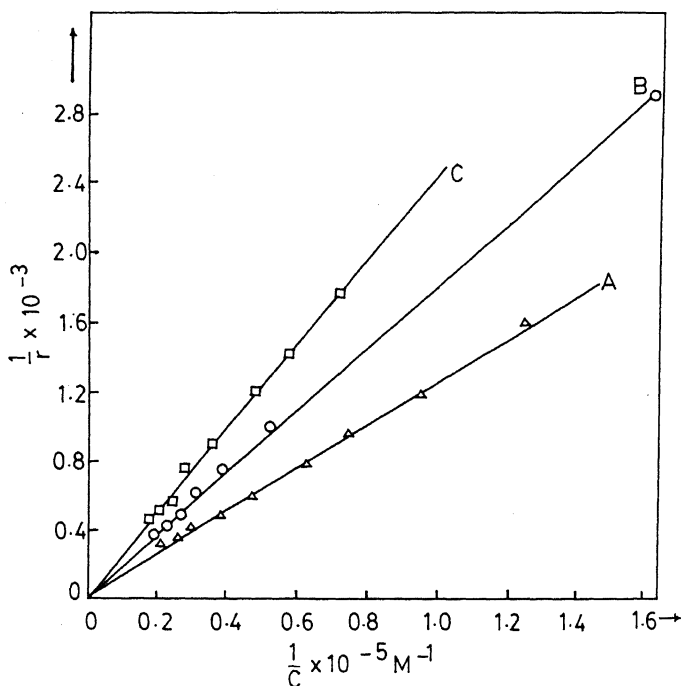


Figure 1. Klotz plot for the ANS-k30 PVP system. [PVP] = $2.25 \times 10^{-2} \text{M}$; 0.05 M buffer, pH 7.1. Determinations at A, 3°C; B, 25°C; C, 40°C.

Table 1. Binding parameters of the ANS-PVP system. [PVP] = 2.25×10^{-2} M; 0.05 M buffer pH 7.1.

Temperature (°C)	k30 PVP			k90 PVP		
	$\frac{1}{n}$	nK (M ⁻¹)	$K \times 10^{-3}$ (M ⁻¹)	$\frac{1}{n}$	nK (M ⁻¹)	$K \times 10^{-3}$ (M ⁻¹)
3		80.79	2.88 ^b		149.63	13.11
25	35.63 ^a	56.68	2.02	89.24	91.24	8.14
40		42.48	1.51		—	—

^a Temperature coefficient on n is small. Hence a mean $1/n$ value has been given.^b K values have been calculated using mean n values.**Table 2.** Thermodynamic parameters of the ANS-PVP system.

k30 PVP			k90 PVP		
ΔF^0 cal/mol	ΔH^0 cal/mol	ΔS^0 eu/mol	ΔF^0 cal/mol	ΔH^0 cal/mol	ΔS^0 eu/mol
-4507	-3050	4.89	-5332	-3968	4.58

Parameters were calculated using K values.**Table 3.** Effect of urea and palmitic acid on binding. [k30 PVP] = 3.6×10^{-3} M; pH 7.1; Temperature 25°C.

[ANS] ₀ (μM)	$r \times 10^3$		
	PVP + 2 M urea	PVP only	PVP + 20 μM palmitic acid
5	0.20	0.26	0.35
35	1.88	1.98	2.63
50	2.57	2.84	3.69
60	3.05	3.44	4.39
70	4.00	4.51	4.77
75	4.20	4.78	5.69

[ANS]₀ = initial ANS concentration.

Limiting viscosity numbers (intrinsic viscosities) of k30 PVP solution in buffer and in the presence of ANS of three different concentrations were measured from the intercept of a plot of reduced viscosity vs. concentration, using

$$[\eta]_{\text{int}} = [\eta_{\text{red}}]_{c \rightarrow 0} \quad (2)$$

Table 4 presents these values.

Figure 2 shows the fluorescence emission spectra of the ANS-k30 PVP complex in the presence and absence of the additives, the complex being excited at 370 nm. To minimise absorption (< 0.02) at the exciting wavelength, the concentrations of PVP and ANS were maintained as low as possible in the fluorescence experiments. For comparison, both fluorescence and dialysis experiments carried out to study the effect of additives used the same PVP concentration.

Table 4. Limiting viscosity numbers (intrinsic viscosities) of k30 PVP. Temperature 30°C; 0.05 M buffer, pH 7.1.

Sample	$[\eta]_{\text{int}}$ ml/g
PVP in buffer alone	21.22
PVP + 10 μM ANS	20.51
PVP + 40 μM ANS	21.58
PVP + 80 μM ANS	22.37

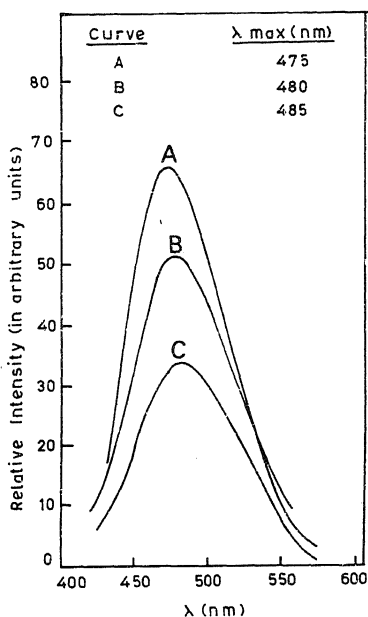


Figure 2. Fluorescence emission spectra of ANS-k30 PVP complex. Excitation wavelength = 370 nm; $[\text{PVP}] = 3.6 \times 10^{-3} \text{ M}$; $[\text{ANS}] = 10 \mu\text{M}$; pH 7.1. A, PVP + ANS + 20 μM palmitic acid; B, PVP + ANS; C, PVP + ANS + 2 M urea.

Figure 3 displays the spectra of k30 PVP ($3.6 \times 10^{-4} \text{ M}$) in buffer solution (A) and in the presence of 20 μM ANS (B), the latter recorded using the same ANS solution as blank. In figure 4 curves A, B and C are spectra of ANS (20 μM) in buffer, in $3.6 \times 10^{-4} \text{ M}$ k30 PVP and in 9:1 (v:v) buffer-methanol mixture respectively. As before, to record the spectrum of ANS in presence of PVP, the same PVP solution was kept as reference.

3.1 Affinity and interacting forces

From the values of the intrinsic binding constants in table 1, we infer that both k30 and k90 PVP samples have moderately strong affinity towards ANS. This affinity, as evident from the data in table 2, comes from the large negative free energy

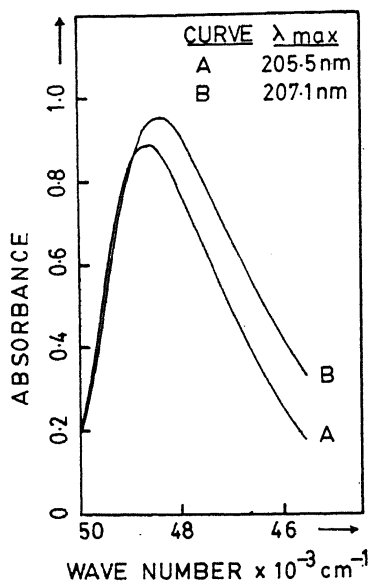


Figure 3. Spectra of k30 PVP in A, buffer solution; B, 20 μ M ANS. [PVP] = 3.6×10^{-4} M; 0.05 M buffer, pH 7.1.

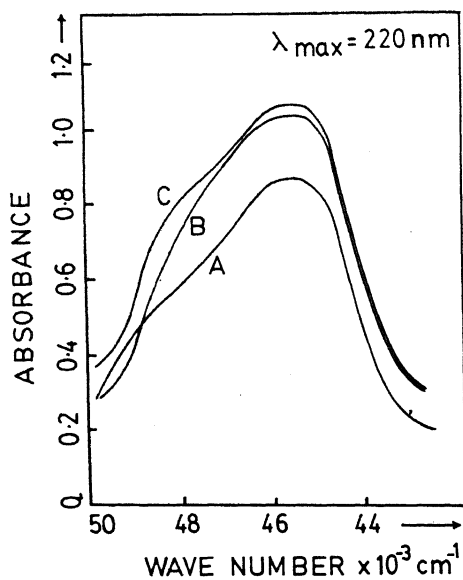
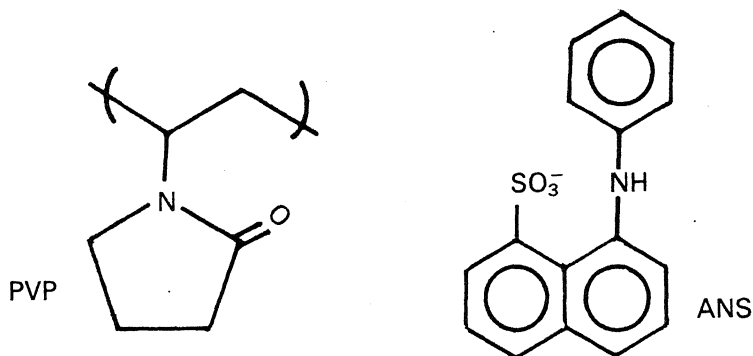


Figure 4. Spectra of ANS in A, buffer solution; B, 3.6×10^{-4} M k30 PVP; C 9 : 1 (v : v) buffer-methanol mixture. [ANS] = 20 μ M; 0.05 M buffer, pH 7.1.

change occurring in the binding process. Both negative enthalpy and positive entropy contribute to the observed free energy change. Thus the binding process is an energetically and entropically favoured one.

To explain the observed binding affinity, we have to consider the structural features of PVP and of ANS.



In PVP, the repeating unit is made up of two kinds of groups, i.e., the non-polar methylene and methine (CH) groups and the polar carbonyl group, with one hetero atom N at the centre of the pyrrolidone ring. The N and O atoms in the amide linkage carry fractional positive and negative charges respectively due to keto-enol tautomerism. The ligand molecule ANS is composed of non-polar aromatic rings with π electron cloud and one polar sulphonate group as the substituent. From the structures, the operation of the following forces is possible in the binding system.

- (i) Electrostatic interaction of the ion-dipole type between the sulphonate group in ANS and the amide linkage in PVP.
- (ii) Forces of dipole-induced dipole type between the carbonyl group in PVP and the easily polarisable aromatic rings in ANS.
- (iii) Hydrophobic interaction between the aromatic rings in ANS and the non-polar groups in PVP.

The actual interacting forces which can be inferred from the experimental results are discussed below.

3.2 Absence of ion-dipole forces

Previous studies (McClure and Edelman 1966) on binding of 2-*p*-toluidinonaphthalene-6-sulphonate (TNS, structurally analogous to ANS) to bovine serum albumin have demonstrated that the probe binds to hydrophobic sites in the protein and that the sulphonate group does not play a significant role in binding. In TNS-PVP systems also (Takagishi *et al* 1978; Reeves *et al* 1981) the involvement of the sulphonate group in binding has not been invoked. Even the NMR investigation of the mechanism of binding of ANS to PVP (Kono *et al* 1973) did not reveal anything about the role of this group in binding. An obvious evidence for the non-involvement of this group in binding is as follows. Cross-linked PVP at neutral pH has been observed by us to have absolutely no binding affinity towards aromatic compounds with negatively charged groups, e.g., 1-naphthylacetic acid and naphthalene-1,5-disulphonic acid, whereas ANS, a similar molecule, does bind. This is possible only when the sulphonate group is not involved in binding. A similar situation is expected in the case of water-soluble PVP used in the present study. A possible reason for the non-involvement is the fact that the $> \text{NH}$ and

sulphonate groups of ANS occupy the peri-positions of the naphthalene ring and have been shown to interact with each other (Balasubramanian 1966), thus preventing the sulphonate group from interacting with binding sites. As a result the operation of ion-dipole forces in the binding system may not be feasible.

3.3 Dipole-induced dipole forces and spectral evidence

The negative enthalpy change indicates the existence of energetic forces. But from the foregoing discussion, it seems that the forces of dipole-induced dipole nature originating from the polar carbonyl group in PVP and the easily polarisable π electron cloud in ANS are the predominantly contributing energetic forces. Spectral evidence, illustrated in figures 3 and 4, supports the above conclusion. The changes in the spectral properties of PVP and ANS on adding one component to the other clearly indicate the partial removal of water molecules and hence each provides with the other a less polar environment in the binding site. This point is proved by the spectrum of ANS in buffer-methanol mixture. The $n \rightarrow \pi^*$ transition of the carbonyl group in PVP is red-shifted with increase in intensity (figure 3). This shows that the group not only lies in a relatively less polar environment but also interacts with a non-polar group, i.e., the aromatic rings. The intensity of the $\pi \rightarrow \pi^*$ transition of ANS is enhanced (figure 4) when it binds to PVP. This enhanced intensity is possible only when the π electron cloud is perturbed and this happens when ANS interacts with the pyrrolidone rings of PVP.

3.4 Hydrophobic interaction

Hydrophobic interaction between two non-polar moieties is always associated with positive entropy (Nemethy 1967). Since the binding process in our system also is accompanied by positive entropy, it can be considered as a clear indication of the existence of hydrophobic interaction in the ANS-PVP system. The participating groups are the methylene and methine groups in PVP and the non-polar aromatic rings in ANS. This is supported by the observation that ANS shows fluorescence in k30 PVP solution (3.6×10^{-3} M) but not in a solution of N-methylpyrrolidone, which is a monomer structurally similar to N-vinylpyrrolidone. PVP, because of its very open flexible conformational chain, is able to provide a non-polar environment whereas the N-methylpyrrolidone monomer solution of the same concentration containing only single entities is unable to do so.

3.5 Affinity of k30 and k90 PVP's

To get an idea about the effect of molecular weight on ligand binding, k30 and k90 polymer samples with the same monomer concentration were used. From table 1 we infer that k90 PVP has a 4-fold higher affinity to ANS than does k30 PVP. This can be explained by comparing the values of the thermodynamic parameters of the two systems. ANS-k90 PVP has a lower ΔH^0 value (table 2) but the entropy values of the two systems are more or less the same within the limits of experimental error. This shows that the higher affinity of k90 PVP is mainly due to the energetic forces, the hydrophobic interaction operating to the same extent. This inference can be explained by considering the $1/n$ values. One ANS molecule interacts with 89 monomer units in k90 PVP but only with 36 monomer units in k30 PVP. The

stronger interaction is responsible for the enhanced energetic forces in ANS-k90 PVP resulting in a lower ΔH^0 value. The similarity in contribution of hydrophobic interaction may be due to the similarity of the microenvironments of the binding sites in both the PVP samples. This is found to be true from the observation that in both the PVP solutions, ANS has the same fluorescence emission maximum (480 nm).

3.6 Conformational change

Viscosity can be exploited to detect conformational change in solute molecules. We have obtained 21.22 ml/g as the limiting viscosity number for k30 PVP in buffer at 30°C (table 4) which is quite in agreement with the value of 21.8 ml/g measured in water at 25°C (Molyneux and Vekavakayanondha 1986). Table 4 shows that there is only slight change in limiting viscosity number of PVP on addition of ANS at the concentrations employed. This implies that there is no significant conformational change in PVP on ANS binding and that the monomer units in the binding sites are not in rigid compact arrangement but are still flexible.

3.7 Effect of additives

Two additives, namely, urea and palmitic acid, have been employed in dialysis and fluorescence experiments, at concentrations 2 M and 20 μ M respectively. The very slight solubility of palmitic acid in water prevented us from using a higher concentration. The inferences obtained are interesting because they are helpful in obtaining some knowledge of the microenvironment of the binding sites.

Urea is a three-dimensional water structure breaker and thereby weakens hydrophobic interaction (Nemethy 1967) whereas palmitic acid [$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$] induces a hydrophobic hydration sheath around its molecular cavity because of its lengthy non-polar aliphatic chain. The latter is a more favourable condition for the strong hydrophobic interaction between PVP and ANS. Thus both urea and palmitic acid alter the microenvironment of the binding sites by affecting the iceberg structure of water. From their role, we expect that urea should inhibit ANS binding while palmitic acid should facilitate it. The observed experimental results support this expectation. The affinity for ANS is decreased in the presence of urea while it is increased in the presence of palmitic acid; this is clear from a comparison of the r values given in table 3. The binding of ANS by the fatty acid alone was tested by taking ANS in palmitic acid solution. But the very negligible intrinsic emission of ANS in buffer was not increased in the presence of palmitic acid. This shows clearly that ANS does not bind to the fatty acid and the increase in r value in the presence of the latter is wholly due to the enhanced binding of ANS to PVP.

The additives not only affect the amount of ANS bound by altering the microenvironment but also change the nature of the binding sites, as evident from the results of fluorescence experiments (figure 2). The ANS-k30 PVP complex has a fluorescence emission maximum at 480 nm. The addition of urea red-shifts it to 485 nm with reduction in intensity and increase in band width. But the palmitic acid blue-shifts it to 475 nm with decrease in band-width and increase in intensity. The emission maximum is very sensitive to the probe's environment. Its red-shift with band broadening indicates the existence of the probe in a relatively polar

environment while the blue-shift with band narrowing indicates a non-polar environment. Thus the binding sites on PVP become less non-polar in urea and more non-polar in palmitic acid solutions. This change in the nature of binding sites, as already discussed, is interconnected with the microenvironment, i.e., the ordering and disordering of water.

Acknowledgement

The financial assistance offered by University Grants Commission, New Delhi, to one of the authors (ES) is gratefully acknowledged.

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Crystal structure of hirudonine sulphate – a rare polyamine[†]

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MS received 3 September 1987; revised 30 November 1987

Abstract. Hirudonine sulphate ($C_9H_{23}N_7 \cdot 1.5 H_2SO_4 \cdot 2.5 H_2O$) is triclinic in $P1$ space group with cell constants $a = 7.168(9)$, $b = 14.534(6)$, $c = 11.918(5)$ Å, $\alpha = 110.50(3)$, $\beta = 108.75(6)$ and $\gamma = 79.16(6)^\circ$, $V = 1097(2)$ Å³, $Mr = 421.4$, $Z = 2$, $d_x = 1.358(2)$ g cm⁻³, $d_c = 1.276$ g cm⁻³. MoK_α ($\lambda = 0.7903$ Å), $\mu = 1.94$ cm⁻¹, $F(000) = 436$, $T = 295$ K, $R(F) = 0.144$. The structure was solved by direct methods and refined to a final R factor of 0.144 for 1036 unique reflections. One of the sulphur atoms is in special position and is disordered. The amine molecule is hydrogen-bonded to the sulphate oxygen through water molecules. Water channels are formed at unique places involving water oxygens, amine and sulphate oxygens along the a axis.

Keywords. Polyamines; hirudonine sulphate; water channels.

1. Introduction

Polyamines are low molecular weight, aliphatic nitrogenous bases. Polyamines produced from amino acids by bacteria have pharmacological activity in animals (Fruton and Simmonds 1965). They are present in all cells in large amounts and appear to possess the potentiality of substituting for cations such as K^+ or Mg^{++} that may be in short supply. They are highly regulated and are essential for cell growth and differentiation (Scalabrino and Ferioli 1981, 1982). Polyamines stabilize DNA by bridging the polynucleotide strands of the double helix through hydrogen bonds with phosphates across the grooves (Tsuboi 1964; Liquori *et al* 1967; Stevens 1967; Suevalsky *et al* 1969; Cohen 1971). It has been reported that the polyamine content of the urine of cancer patients is higher than that of healthy persons (Cohen 1971). Several models for binding of polyamines to DNA have been proposed in the past (Tsuboi 1964; Liquori *et al* 1967; Woo *et al* 1979; Vasantha Pattabhi and Chandrasekar 1982). Hirudonine sulphate is a rare polyamine and in view of its importance, the crystal structure analysis of the compound was undertaken as part of the project on studies on polyamines.

2. Experimental

Colourless, thin rectangular, transparent crystals of $0.1 \times 0.2 \times 0.45$ mm were obtained by slow evaporation from a mixture of water and chloroform.

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[†]DCB contribution Number 712.

Three-dimensional intensity data were collected on a Nonius CAD-4 automatic diffractometer using monochromated MoK_α radiation. Due to the poor quality of the crystal, out of 2108 unique reflections collected, 1036 reflections were considered as observed with $I \geq 2\sigma(I)$. One standard reflection (003) was checked for every 100 reflections. Lattice parameters were refined with 17 reflections for the measured 2θ values in the range $3 \leq \theta \leq 27^\circ$. Max $h = 6$, max $k = 13$, max $l = 13$, min $h = 0$, min $k = -16$, min $l = -11$. The data were corrected for polarisation and Lorentz effects but not for absorption.

The structure was solved in the space group $P1$ by direct methods using the program MULTAN80 (Main *et al* 1980). It was noticed that the coordinates of the two amine molecules were related by a centre of inversion and hence the origin was shifted to the centre of symmetry, changing the space group to $P\bar{1}$. A few more cycles of refinement in $P\bar{1}$ using the program SHELX76 (Sheldrick 1976) reduced the R index to 0.20. The special position sulphate oxygens were assigned an occupancy factor of 0.5 and were refined. The site occupancy and thermal parameters were refined alternately. However, the sulphate geometry thus obtained was not satisfactory and the final ΔF map had a residual peak $0.7 \text{ e}\text{\AA}^{-3}$. The R index at this stage is 0.122.

In order to improve the geometry of the sulphate group at special position, bond length- bond angle-constrained refinement was carried out with 0.5 occupancy for sulphate oxygens. The sulphate geometries for both constrained and unconstrained refinements are shown in figure 1. Four water molecules were located from difference Fourier out of which three were disordered with occupancies 0.5, 0.6 and 0.4. It is interesting to note here that the observed density accounts for four water molecules, but in this case their occupancies add up to 2.5 only. Thus the difference in calculated and observed density may be due to the disorder in the molecule which could not be accounted for completely. The amine, sulphate S(2), special position sulphur and one of the water molecules were refined anisotropically and the rest isotropically. The hydrogens were located from ΔF map and checked against stereochemically fixed positions. Out of 31⁺ hydrogens present in the molecule, two hydrogens attached to N(1) and N(15), water hydrogens, and the

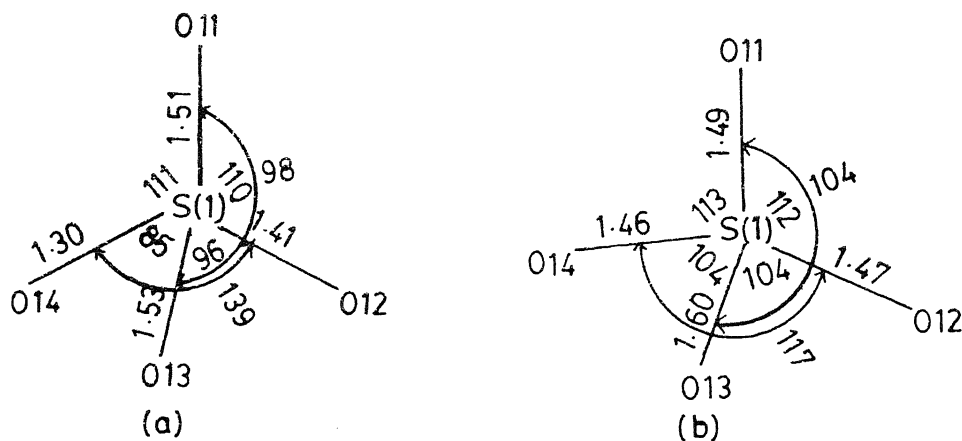


Figure 1. Sulphate geometry (a) constrained and (b) unconstrained.

Table 1. Final fractional positional parameters and equivalent temperature factor ($\text{\AA}^2$) for non-hydrogen atoms with esd's in parentheses.

$$Beq = \frac{8\pi^2}{3} \sum \sum U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Atom	x	y	z	Beq	SOF*
S(2)	0.454(1)	0.0995(5)	0.2805(7)	4.0(3)	
O(21)	0.431(4)	0.204 (1)	0.298 (2)	9 (1)	
O(22)	0.482(5)	0.080 (2)	0.387 (2)	14 (1)	
O(23)	0.628(5)	0.056 (2)	0.243 (3)	14 (2)	
O(24)	0.305(4)	0.050 (2)	0.183 (3)	17 (2)	
N(1)	0.259(3)	0.266 (2)	1.080 (2)	4 (1)	
C(2)	0.252(3)	0.199 (2)	0.966 (2)	3 (1)	
N(3)	0.302(3)	0.104 (2)	0.951 (2)	5 (1)	
N(4)	0.193(3)	0.233 (1)	0.867 (2)	4 (1)	
C(5)	0.156(4)	0.170 (2)	0.741 (2)	4 (1)	
C(6)	0.094(4)	0.231 (2)	0.655 (3)	5 (1)	
C(7)	0.043(4)	0.168 (2)	0.519 (2)	5 (1)	
C(8)	-0.014(4)	0.229 (2)	0.431 (2)	4 (1)	
N(9)	-0.061(3)	0.171 (1)	0.299 (2)	5 (1)	
C(10)	-0.127(4)	0.230 (2)	0.209 (2)	4 (1)	
C(11)	-0.171(4)	0.164 (2)	0.077 (2)	4 (1)	
C(12)	-0.247(4)	0.222 (2)	-0.015 (2)	4 (1)	
N(13)	-0.288(3)	0.156 (1)	-0.140 (2)	4 (1)	
C(14)	-0.346(4)	0.182 (2)	-0.241 (3)	4 (1)	
N(15)	-0.386(3)	0.115 (2)	-0.354 (2)	5 (1)	
N(16)	-0.362(3)	0.278 (2)	-0.234 (2)	6 (1)	
<i>Water oxygens</i>					
Ow(1)	0.501(5)	0.324 (2)	0.537 (2)	11 (1)	1.0
Ow(2)	0.63 (1)	0.476 (5)	0.196 (6)	13 (2)	0.5
Ow(3)	-0.18 (1)	0.494 (6)	-0.348 (9)	19 (1)	0.6
Ow(4)	0.23 (1)	0.512 (6)	0.598 (7)	14 (1)	0.4
S(1)	0.0	0.5	0.0	13 (1)	
<i>Sulphate oxygens, unconstrained</i>					
O(11)	-0.184(6)	0.457(5)	-0.011(6)	25(1)	
O(12)	0.095(6)	0.435(5)	-0.089(3)	7(1)	
O(13)	0.136(8)	0.470(5)	0.112(4)	16(2)	
O(14)	0.011(8)	0.589(2)	0.078(3)	6(1)	
<i>Sulphate oxygens, constrained</i>					
O(11)	-0.205(4)	0.475(4)	0.025(5)	18(1)	
O(12)	0.089(6)	0.442(3)	-0.101(3)	12(1)	
O(13)	0.126(6)	0.462(3)	0.115(3)	15(2)	
O(14)	0.021(7)	0.606(1)	0.048(4)	15(2)	

* Site occupancy factor.

ones belonging to the sulphate groups could not be located. Hydrogens were not refined and were included in the structure factor calculation only. As the quality of the data was very poor, the accuracy of the results obtained is restricted. Unit weighting scheme was applied as the individual weighting scheme based on counting statistics did not show any improvement. The final R index is 0.144. Final

difference Fourier map had no peaks greater than $0.6 \text{ e}\text{\AA}^{-3}$. Final (shift/e.s.d.) mean = 0.3. Scattering factors are as given in SHELX76. The fractional positional parameters with equivalent isotropic temperature factors are given in table 1 and anisotropic thermal parameters in table 2.

3. Discussion

The bond lengths and angles are given in figure 2. Figure 3 gives the ORTEP diagram (Johnson 1965) for the thermal ellipsoids drawn at 50% probability level. The bond lengths and bond angles in the putrescine moiety are in good agreement with the values reported for agmatine and arcaine. The average values C–C 1.51(4), C–N 1.44(3) Å and C–C–C 112(2), N–C–C 112(2)° are in good agreement with the values 1.48(2), 1.51(2) Å and 113(2), 112(2)° in arcaine sulphate (Thailambal *et al* 1985) and 1.491(6), 1.525(6) Å and 109.7(5), 110.5(5)° in agmatine sulphate (Chandrasekar *et al* 1982). The average C–N distance 1.34(4) Å in the guanidyl group compares well with the value 1.35(2) Å in arcaine sulphate and 1.333(3) Å in agmatine sulphate. The guanidyl groups and the butylamine segment are planar. The dihedral angle between the guanidyl groups and the

Table 2. Anisotropic thermal coefficients ($\times 10^3$) for non-hydrogen atoms with esd's in parentheses.

$$\text{Temperature} = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	157(20)	157(10)	157(10)	13(10)	44(10)	49(10)
S(2)	80(6)	31(4)	32(4)	10(4)	12(4)	8(3)
O(21)	198(28)	33(12)	87(16)	30(14)	13(16)	22(11)
O(22)	369(47)	78(18)	61(15)	57(22)	104(21)	7(13)
O(23)	257(36)	49(16)	253(35)	15(19)	209(32)	-17(18)
O(24)	138(27)	49(15)	265(35)	30(16)	-153(27)	22(19)
N(1)	35(15)	65(15)	52(14)	3(11)	17(11)	4(12)
C(2)	26(17)	52(18)	52(19)	4(14)	12(14)	19(16)
N(3)	69(19)	48(16)	87(17)	15(13)	43(14)	29(13)
N(4)	60(17)	33(12)	47(14)	8(11)	11(11)	8(11)
C(5)	52(20)	54(18)	44(17)	7(15)	19(14)	7(15)
C(6)	58(22)	45(17)	70(21)	13(15)	26(16)	18(15)
C(7)	83(22)	60(19)	52(19)	9(16)	32(15)	15(16)
C(8)	50(19)	78(21)	37(17)	4(16)	25(13)	6(15)
N(9)	86(19)	38(13)	56(15)	21(12)	31(12)	18(11)
C(10)	48(19)	48(16)	65(19)	-17(14)	17(14)	21(15)
C(11)	47(19)	49(16)	52(18)	17(14)	13(14)	16(14)
C(12)	22(17)	71(19)	59(18)	5(14)	16(13)	19(16)
N(13)	56(16)	41(12)	48(15)	15(11)	25(12)	-1(12)
C(14)	34(19)	74(23)	49(21)	-2(16)	21(15)	23(19)
N(15)	67(18)	77(17)	45(14)	7(14)	23(12)	23(13)
N(16)	64(19)	61(17)	91(19)	11(14)	22(14)	29(15)
Ow(1)	221(33)	85(18)	135(23)	5(19)	72(22)	22(16)

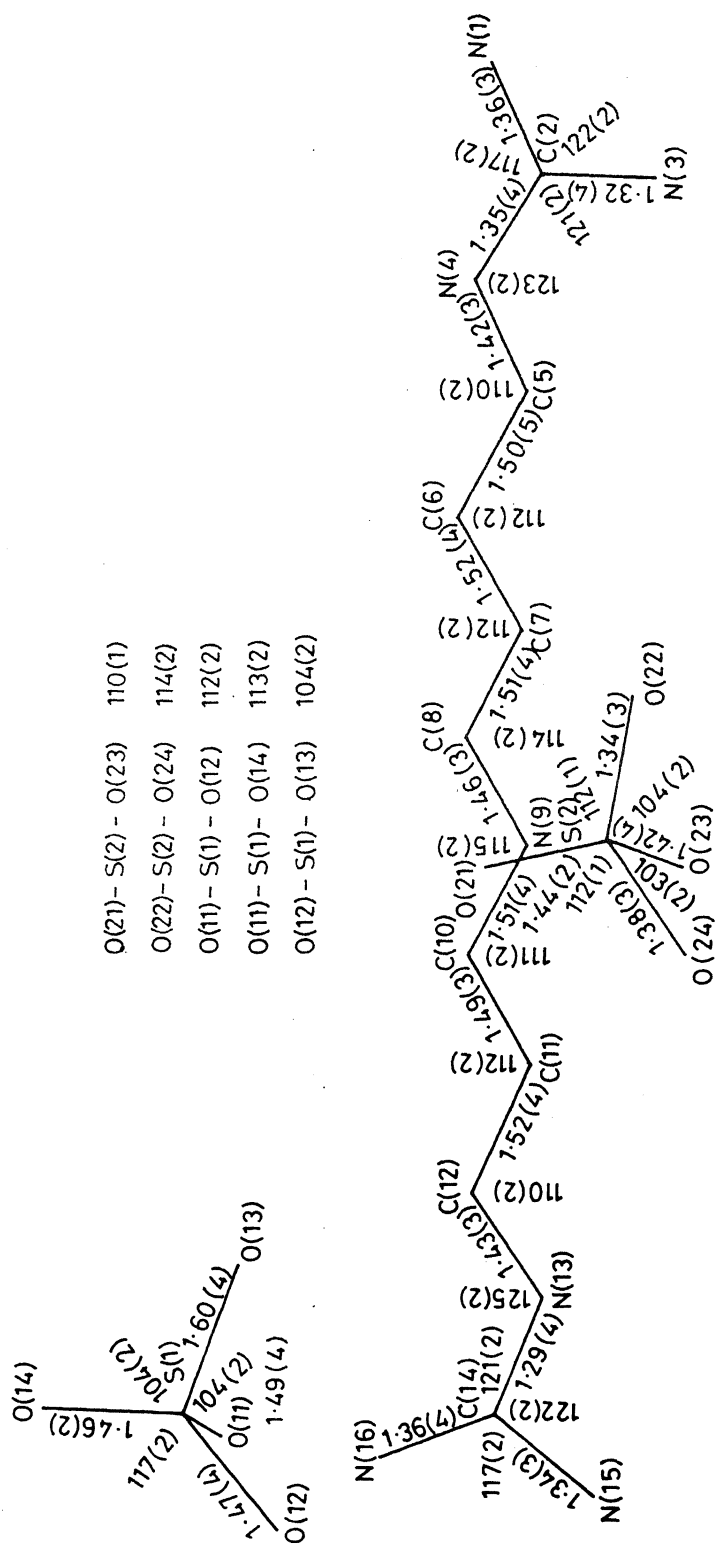


Figure 2. Bond lengths and bond angles involving non-hydrogen atoms.

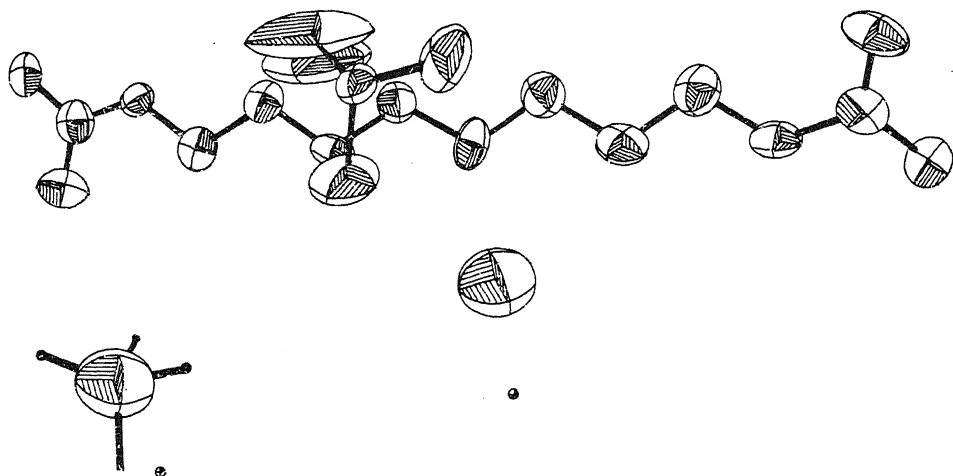


Figure 3. ORTEP diagram for the thermal ellipsoids drawn at 50% probability level.

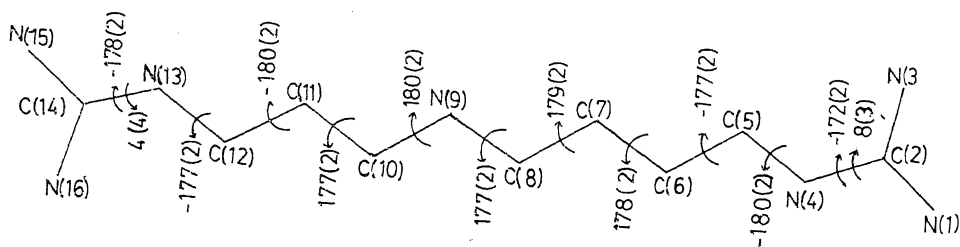


Figure 4. Important torsion angles observed in the amine molecule.

butylamine segment are $9(2)^\circ$ and $127(2)^\circ$. The amine molecule as a whole is in all-*trans* conformation (figure 4). The sulphate S(2) is in a regular tetrahedral geometry with an average S–O distance of $1.39(2)$ Å and O–S–O of $109(1)^\circ$. The oxygens of the sulphate group S(1) are highly disordered with an average distance of $1.44(4)$ Å and O–S–O of $107(2)^\circ$ in the unconstrained refinement; in the constrained refinement the bond lengths vary between $1.46(4)$ and $1.60(4)$ Å and the bond angles between $104(2)$ and $117(2)^\circ$.

The structure exhibits a layerwise packing with the zig-zag amine molecules arranged in planes parallel to the *bc* plane. The water sulphate hydrogen bond network is interleaved between the symmetry-related amine molecules along the *b* axis. All the nine protons available in the amine molecule are involved in hydrogen bonding. The sulphate oxygen O(21) is linked to the water oxygen Ow(1) through a hydrogen bond and Ow(1) is in turn hydrogen-bonded to Ow(4). Though the structure is well stabilized by hydrogen bond network, it shows holes in unique positions, e.g. a water channel involving N(1)...O(21), O(21)...Ow(1), Ow(1)...Ow(4), Ow(4)...Ow(3), Ow(3)...O(13), O(13)...N(1) is formed along the *a* axis. The possible hydrogen bonds are given in table 3. The molecular packing is shown in figure 5.

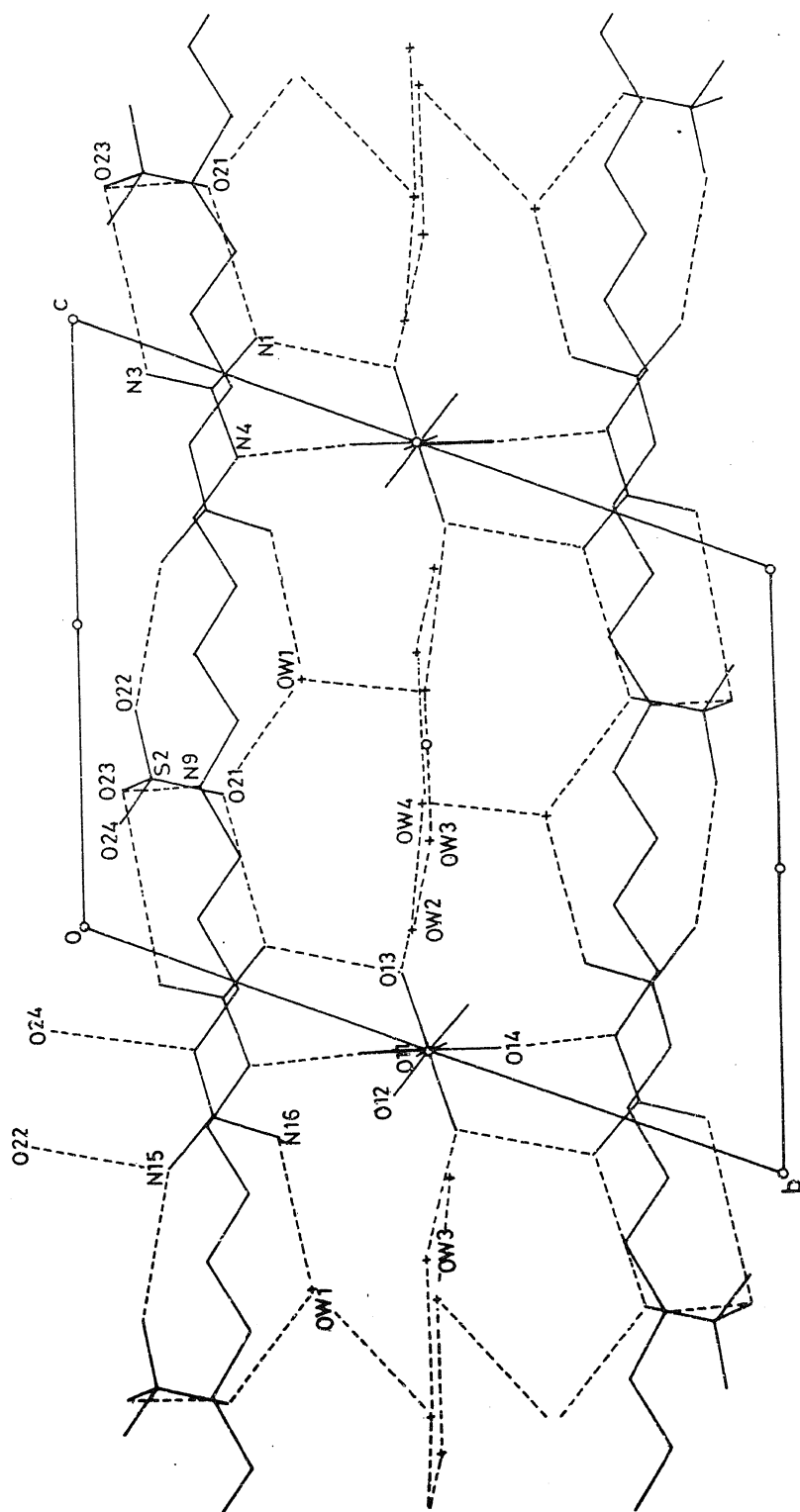


Figure 5. Packing of the molecules down *a* axis in the unit cell and hydrogen bonding scheme.

Table 3. Possible hydrogen bonds.

Contact	Symmetry	Distance (Å)
Ow(4)...Ow(1)	x, y, z	2.91(7)
Ow(1)...O(21)	x, y, z	2.71(3)
O(23)...N(9)	$1+x, y, z$	2.81(4)
N(1)...O(13)	$x, y, 1+z$	2.86(7)
N(1)...O(21)	$x, y, 1+z$	2.87(3)
N(4)...O(12)	$x, y, 1+z$	2.80(4)
Ow(1)...N(16)	$1+x, y, 1+z$	2.86(4)
O(22)...N(15)	$1+x, y, 1+z$	2.81(3)
O(13)...Ow(3)	$-x, 1-y, -z$	2.60(6)
Ow(2)...Ow(4)	$1-x, 1-y, 1-z$	2.35(4)
Ow(4)...Ow(3)	$-x, 1-y, -z$	2.80(4)
O(14)...N(4)	$-x, 1-y, 1-z$	2.71(3)
O(22)...N(15)	$-x, -y, -z$	2.91(4)
O(23)...N(3)	$1-x, -y, 1-z$	2.75(4)
O(24)...N(13)	$-x, -y, -z$	2.87(4)

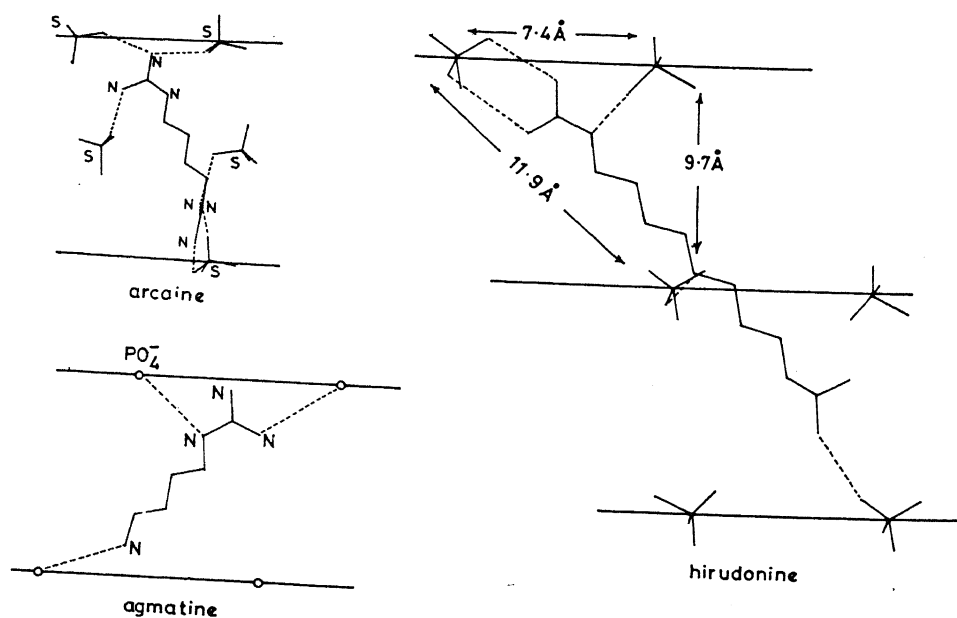


Figure 6. Possible mode of binding for hirudonine, arcaine and agmatine.

The configurational similarities between the sulphate and phosphate ions make it possible to extrapolate the observations made in hirudonine sulphate to the possible mode of binding with nucleotide. The inter-sulphate distance of $7.17 \text{ \AA}$ along the a axis and $7.43 \text{ \AA}$ between those hydrogen bonded to the same guanidyl group can be compared with the distance of $7.3 \text{ \AA}$ between the successive phosphate groups along the helix in polynucleotides (Langridge *et al* 1960). The

hirudonine molecules have a packing similar to other polyamines. This is made possible by the presence of an additional sulphate group at special position. The two halves of the molecules maintain a geometry such that they can mimic the binding of putrescine and agmatine with DNA. Hence it can be concluded that there is a possibility of hirudonine binding to DNA across the narrow groove making two hydrogen bonds with one strand and one with the other as in the case of arcaïne and agmatine (figure 6).

Acknowledgement

One of the authors (MN) acknowledges the financial support provided by the Council of Scientific and Industrial Research, New Delhi.

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Enthalpies of hydrogen-bonded butylamine-chloroform complexes[†]

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MS received 18 June 1987; revised 13 October 1987

Abstract. Enthalpies of mixing of isomeric butylamine with chloroform were determined at 30°C by a Calvet-type microcalorimeter. The system showed highly exothermic behaviour due to hydrogen-bonded complex formation on mixing. The enthalpies of complex formation were calculated by means of a thermo-chemical cycle and the values vary from 1-aminobutane to 2-amino-2-propane complexes.

Keywords. calorimetry; amine-chloroform complexes; binary systems; enthalpy of complex.

1. Introduction

The energies of hydrogen-bonded complexes depend on the electron densities of proton-acceptor and -donor atoms of the H-bond forming molecules. Steric and electromeric effects also play important roles in strengthening or weakening the H-bond (Geisler *et al* 1971). The enthalpies of H-bonded complexes therefore depend on the functional groups as well as the structure of complex-forming molecules. In our earlier work we have determined the enthalpies of H-bonded complexes between $\text{NH}_2 \dots \text{OH}$, $\text{NH} \dots \text{OH}$, $\text{N} \dots \text{OH}$ groups and also studied the isomeric effect on the strengths of H-bonds (Pradhan and Mathur 1979; Pradhan 1981; Pradhan and Pathak 1986). In the present communication the work on the enthalpies of complex formation between isomeric butylamines and chloroform has been reported.

2. Experimental

The isomeric butylamines (S.D. Chemicals, AR grade) were purified by fractional distillation and the chloroform (S.D. Chemicals, AR grade) was purified by the standard method (Riddick and Bunger 1970). All the compounds were dried over freshly activated molecular sieves. The heats of mixing were determined by heat flux Calvet microcalorimeter (C-80 Setaram model) at 30°C.

[†]NCL Communication No. 4255

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3. Results and discussion

The enthalpies of mixing of 1-aminobutane, 1-amino-2-methyl propane, 2-amino-butane and 2-amino-2-methyl propane with chloroform have been given in table 1. The values have been rounded to tens of joules. The data is fitted by means of the least square method in a Redlich-Kister equation:

$$\Delta H = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + E(x_1 - x_2)^3]. \quad (1)$$

The Redlich-Kister parameters along with the standard deviations have been given in table 2. The enthalpies of mixing as a function of mole fraction of amine have been represented in figure 1.

All the four systems exhibit highly exothermic characteristics due to the formation of hydrogen-bonded complexes between the amine and chloroform molecules as shown in figure 2.

The enthalpies of complex formation have been calculated by means of a thermochemical cycle (Murakami and Fujishiro 1966). The ultimate equation from the cycle is

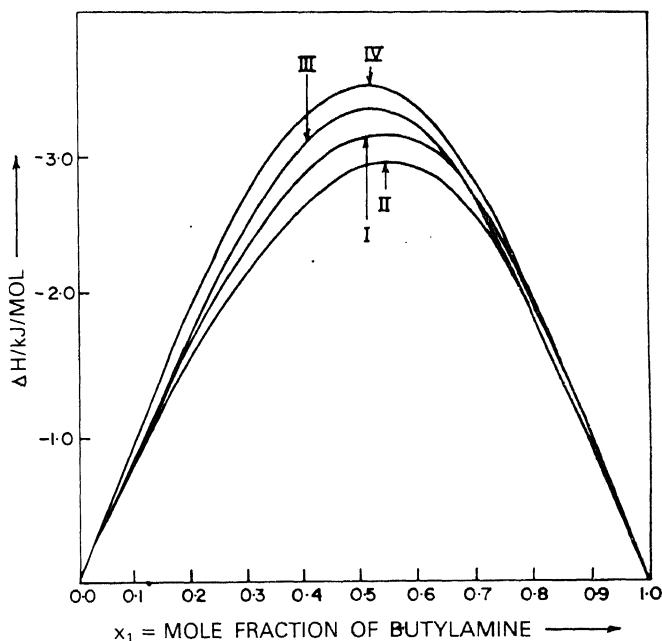
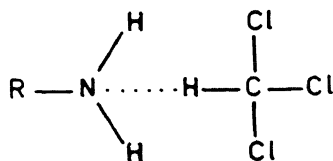
$$\Delta H_c = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d, \quad (2)$$

Table 1. The enthalpies of mixing of isomeric butylamine (1)-chloroform (2) systems at 30°C.

(mole fraction of amine)	ΔH (J/mole)	x_1 (mole fraction of amine)	ΔH (J/mole)
1-Aminobutane (1) + chloroform (2)		2-Aminobutane (1) + chloroform (2)	
0.0898	-820	0.0909	-800
0.2056	-1770	0.1577	-1420
0.3030	-2350	0.2678	-2270
0.4000	-2830	0.2908	-2470
0.4963	-3140	0.3269	-2710
0.5908	-3130	0.4700	-3290
0.6718	-2850	0.5192	-3320
0.7007	-2680	0.5985	-3210
0.7959	-2000	0.7007	-2690
0.9074	-940	0.7397	-2420
		0.8000	-1870
1-Amino-2-methylpropane (1) + chloroform (2)		0.8565	-1340
0.1008	-890	0.9026	-880
0.2000	-1590	2-Amino-2-methyl propane (1) + chloroform (2)	
0.3110	-2210	0.0782	-800
0.3965	-2660	0.1977	-1950
0.5001	-2920	0.3052	-2780
0.5837	-2920	0.3082	-2790
0.6647	-2700	0.4058	-3280
0.7364	-2350	0.4827	-3470
0.7919	-1920	0.5438	-3440
0.8000	-1880	0.6058	-3290
0.8125	-1800	0.7031	-2800
0.8618	-1320	0.8148	-1870
0.8837	-1140	0.9078	-890
0.9025	-910		

Table 2. The Redlick-Kister parameters for enthalpies of mixing of isomeric butylamine(1)-chloroform(2) systems at 30°C.

System	<i>B</i> (J/mole)	<i>C</i> (J/mole)	<i>D</i> (J/mole)	<i>E</i> (J/mole)	Standard deviation (J/mole)
1-Aminobutane + CHCl ₃	-12498.9	-2422.5	2825.1	2672.4	21
1-Amino-2-methyl propane + CHCl ₃	-11639.7	-2846.0	2244.7	3686.9	18
2-Aminobutane + CHCl ₃	-13280.1	-1301.6	5207.4	1848.6	13
2-Amino-2-methyl propane + CHCl ₃	-13913.3	-716.4	4377.6	1581.4	12

**Figure 1.** ΔH vs. x_1 plots for isomeric butylamine (1)-chloroform (2) systems. I-1-amino butane; II-1-amino-2-methyl propane; III-2-aminobutane; IV-2-amino-2-methyl propane.**Figure 2.** The amino-chloroform hydrogen-bonded complex.

where ΔH_c is the enthalpy of complex formation, ΔH_1 and ΔH_2 are respectively the partial molar enthalpies of amine and chloroform in a non-polar solvent i.e. *n*-hexane, ΔH_3 is the partial molar enthalpy of mixing of amine in chloroform and ΔH_4^d is the dipolar stabilisation energy of the complex.

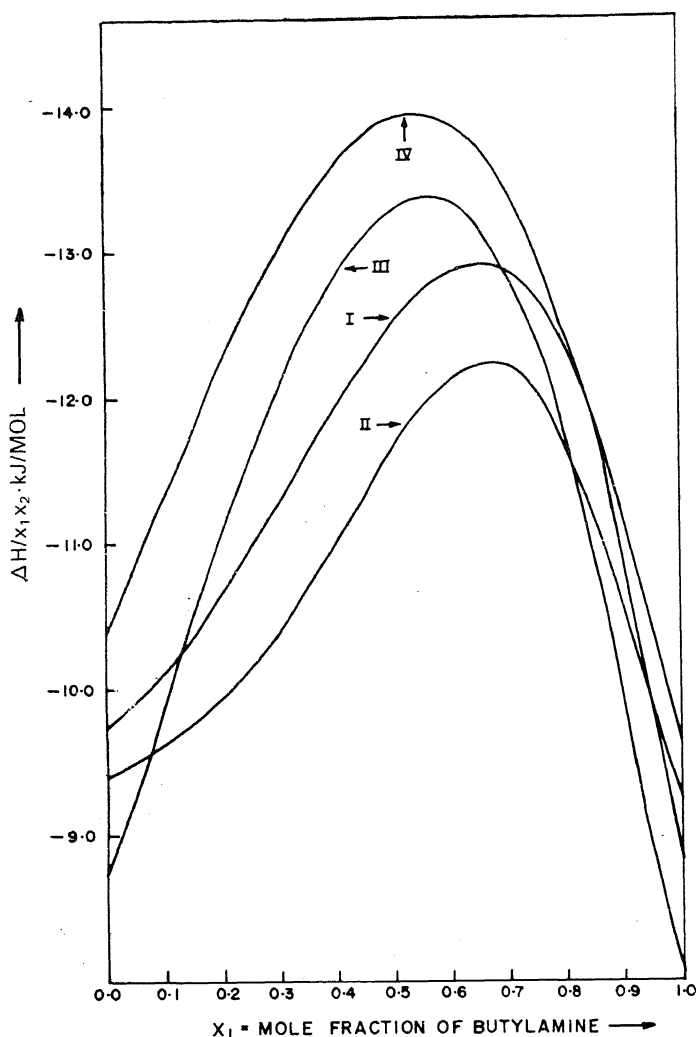


Figure 3. $\Delta H_1/x_1x_2$ vs. x_1 plots for isomeric butylamine (1)-chloroform (2) systems. I-1-aminobutane; II-1-amino-2-methyl propane; III-2-aminobutane; IV-2-amino-2-methyl propane.

The ΔH_4^d is the difference between the dipolar stabilisation enthalpies of the complex in non-polar (*n*-hexane) and polar (chloroform) media.

The dipolar stabilisation enthalpy of a dipole in medium '*i*' is calculated from the free energy of dipole stabilisation, which is given by (Buttcher 1952)

$$\Delta G_i = -1/2 f \cdot \mu^2 (1 - \alpha f). \quad (3)$$

the value of f is given by the expression

$$f = 2(\epsilon - 1)/a^3 (2\epsilon + 1), \quad (4)$$

where ' ϵ ' is the dielectric constant ' a ' is the radius and ' α ' is molecular polarizability.

The values of ΔH_1 are taken from our previous work (Pradhan and Mathur

Table 3. The enthalpies of complex formations of isomeric butylamine-chloroform complexes calculated by (2).

System	ΔH_1 (kJ/mole)	ΔH_2 (kJ/mole)	ΔH_3 (kJ/mole)	ΔH_4^d (kJ/mole)	ΔH_c (kJ/mole)
1-Aminobutane- <i>n</i> -hexane	8.4 ± 0.3	—	—	—	—
1-Amino-2-methylpropane- <i>n</i> -hexane	7.5 ± 0.3	—	—	—	—
2-Aminobutane- <i>n</i> -hexane	6.6 ± 0.3	—	—	—	—
2-Amino-2-methylpropane- <i>n</i> -hexane	4.9 ± 0.3	—	—	—	—
Chloroform- <i>c</i> -hexane		2.6 ± 0.05			
1-Aminobutane-chloroform			-9.7 ± 0.1	1.2	-19.5 ± 0.5
1-Amino-2-methylpropane-chloroform			-9.4 ± 0.1	1.2	-18.3 ± 0.5
2-Aminobutane-chloroform			-8.7 ± 0.1	1.2	-16.7 ± 0.5
2-Amino-2-methylpropane-chloroform			-10.3 ± 0.1	1.2	-16.6 ± 0.5

1978), while the ΔH_2 value is obtained from the literature data on heats of mixing of chloroform with *c*-hexane (Nagata *et al* 1980).

The ΔH_3 values are obtained from the extrapolation of $\Delta H/x_1x_2$ vs. x_1 curves to zero mole fraction of amine. The ΔH values at different mole fractions of amine (x_1) were obtained from the Redlick-Kister equation (1) and the $\Delta H/x_1x_2$ vs. x_1 curves are represented in figure 3.

The values of ΔH_1 , ΔH_2 , ΔH_3 , ΔH_4^d and the ultimate values of enthalpies of amine-chloroform complex formation are given in table 3. The enthalpies of complex formation between the isomeric amine-chloroform changes in the order-

n-amine > iso-amine > sec-amine > tert-amine

Our previous work on amine-alcohol complex formation indicated that a complex between a tertiary and a normal molecule is slightly stronger than that between two normal molecules due to the electromeric effect of CH_3 groups on the α carbon atom. However, we have also found that when two tertiary molecules interact, the strength of H-bonded complexes decreases due to the dominance of the steric effect. In the presently studied systems, the tertiary amine-chloroform complexes are weaker by about 3 kJ/mole as compared to normal amine-chloroform complexes. It seems therefore that there is a steric repulsion between the CH_3 groups of a tertiary molecule and the three chlorine atoms of chloroform and the system behaves like a two-tertiary molecular system.

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Conformations of dibenzylideneacetone: An IR spectroscopic study

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MS received 9 October 1987

Abstract. The conformational analysis of dibenzylideneacetone has been carried out using IR spectroscopy. Appearance of a triplet C=O band is attributed to the coexistence of three conformers viz *s-cis*, *cis*, *s-cis*, *trans* and nonplanar *s-trans*, *trans* in contrast to the earlier findings which showed the existence of only two conformers. The relative proportions of the conformers are in the order *s-cis*, *trans* > nonplanar *s-trans*, *trans* > *s-cis*, *cis* in less polar solvents and nonplanar *s-trans*, *trans* > *s-cis*, *trans* > *s-cis*, *cis* in more polar solvents.

Keywords. Dibenzylideneacetone; triplet C=O band; skew conformation; polarity of the conformers; stability of conformers.

1. Introduction

Conformational analysis of dibenzylideneacetone (DBA) assumed greater importance in view of its ability to form a novel series of zerovalent transition metal complexes because of its existence in several isomeric forms (Takahashi *et al* 1970; Moseley and Maitlis 1971; Ukai *et al* 1974). By virtue of the existence of two degrees of rotational freedom imparted by two single bonds between the olefin and carbonyl group, three conformations viz *s-cis*, *cis*, *s-cis*, *trans* and *s-trans*, *trans* are possible for DBA (figure 1).

A number of attempts have been made earlier to study the conformations of DBA, using different methods viz. molar polarizabilities and Kerr constants (Bramley and Le Fevre 1962), dipole moments (Bentley *et al* 1949; Tsukerman *et al* 1968), NMR (Tanaka *et al* 1978) and UV spectroscopy (Hoshi *et al* 1986).

From Kerr constants and dipole moments study DBA was shown to exist in only one form (*s-cis*, *cis*). Subsequent study of dipole moments by Tsukerman *et al* (1968) indicated the existence of more than one conformation which was supported by the two C=O bands observed in the IR spectrum. By a study of NMR spectra and INDO molecular orbital calculations Tanaka *et al* (1978) came to the conclusion that DBA contains a large proportion of the *s-cis*, *cis* with a small proportion of *s-cis*, *trans* form. Hoshi *et al* (1986) who studied the UV absorption spectra of DBA at room temperature and at 101 K, concluded that the *s-cis*, *cis*

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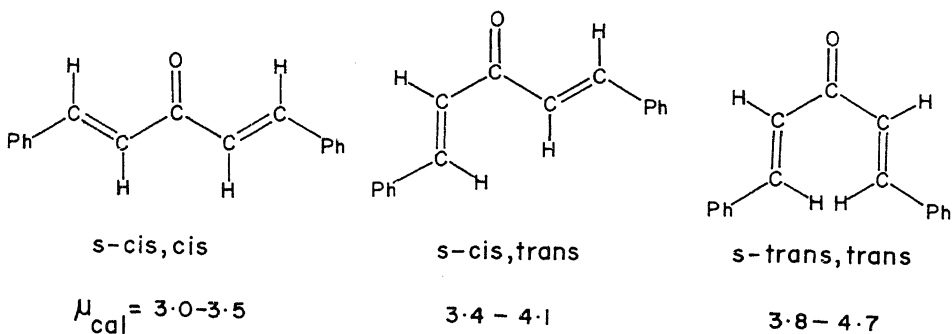


Figure 1. The three possible conformations of dibenzylideneacetone.

conformer is nonplanar at room temperature and attains planarity at low temperatures.

When the IR spectrum of DBA was recorded in our laboratory in connection with a study of its metal complexes three carbonyl bands were observed in contrast to the earlier report (Tsukerman *et al* 1968). This prompted a detailed study of the conformations of this compound. To distinguish between the different conformers, the IR spectra were recorded in solvents of different dielectric constants. The relative proportions of the conformers were determined from the relative intensities of the bands.

2. Experimental

2.1 Materials

DBA was prepared by the aldol condensation in alkaline medium, from benzaldehyde and acetone in 2:1 molar ratio, in ethanol (Vogel 1970). The yellow solid obtained was recrystallized twice from ethyl acetate and thrice from methanol and was TLC pure, m.p. 114°C. The solvents were purified and freshly distilled before use and the middle fractions only were collected.

2.2 Measurement of the spectra

The IR spectra of equimolar solutions (M/20) of the sample in solvents of varied dielectric constants were recorded on a Shimadzu-400 grating double beam spectrophotometer at 28°C using NaCl matched cells of 1 mm path length. The wavenumber scale was expanded by a factor of four and the spectra were calibrated by using the polystyrene film. Extensive overlap of the three carbonyl bands prevented the measurements of their integrated intensities. The relative populations of the different conformers were therefore estimated by measuring the apparent optical densities of the C=O bands as was done in many investigations earlier (Erskine and Waight 1960; Hayes and Timmons 1968; Subrahmanyam *et al* 1980). The positions of the C=O bands together with their relative apparent optical densities are presented in table 1.

Table 1. Stretching frequencies (cm^{-1}) and the relative intensities (A) of the carbonyl bands of dibenzylideneacetone in different solvents,

$$A = \epsilon_{\text{C=O}}(x) / (\epsilon_{\text{C=O}}(\text{I}) + \epsilon_{\text{C=O}}(\text{II}) + \epsilon_{\text{C=O}}(\text{III}))$$

	CCl_4	CHCl_3	CH_2Cl_2
C=O (I)	1676 (0.2107)	1671 (0.1750)	1674 (0.1644)
C=O (II)	1655 (0.4676)	1653 (0.4270)	1654 (0.3920)
C=O (III)	1650 (0.3216)	1648 (0.3970)	1649 (0.4430)

3. Results and discussions

The IR spectrum of DBA in CCl_4 exhibited three C=O bands at 1676, 1655 and 1650 cm^{-1} . The first two bands were reported earlier and the frequencies of the two agreed with the values reported. They are distinct and well-defined; the third, however, appeared as an inflexion on the second band. The relative intensities of the three bands were found to vary with the change in the polarity of the solvent showing that the three C=O bands correspond to the three different conformers in equilibrium. The *s-cis*, *cis* conformer may be considered as similar to the *s-cis* form of benzylideneacetophenone with an additional *s-cis* ethylenic double bond in cross conjugation. The carbonyl frequency of this conformer is expected to be higher than that of the *s-cis* form of benzylideneacetophenone as the C=O frequency is enhanced by the interaction through space, of the C=O and C=C π electrons (Erskine and Waight 1960). This becomes evident when the frequencies of benzophenone (1664 cm^{-1}) and *s-cis* benzylideneacetophenone (1670 cm^{-1}) are compared. So the band at 1676 cm^{-1} is assigned to the *s-cis*, *cis* conformation.

The *s-cis*, *trans* conformer may be treated as the *s-cis* form of benzylideneacetophenone with an additional conjugation of an *s-trans* C=C bond. The frequency of this is expected to be lower than that of the *s-cis* form of benzylideneacetophenone as *trans* conjugation often produces a lowering of C=O frequency. This is evident from the frequencies of benzophenone (1664 cm^{-1}) and *s-trans* benzylideneacetophenone (1648 cm^{-1}). The *s-trans* conjugation thus causes a lowering of C=O frequency by 16 cm^{-1} . If the same effect prevails in the *s-cis*, *trans* conformer, the C=O frequency of this compound should be around 1654 cm^{-1} ($1670 \text{ cm}^{-1} - 16 \text{ cm}^{-1}$). The *s-cis*, *trans* conformer may also be considered the *s-trans* form of benzylideneacetophenone with an additional conjugation of the *s-cis* double bond which raises the frequency by 6 cm^{-1} . Then it may have a frequency closer to that of the *s-trans* form of benzylideneacetophenone (1648 cm^{-1}) with an upward shift of 6 cm^{-1} . Either way, the carbonyl frequency of this conformer is nearly 1654 cm^{-1} . The band observed at 1655 cm^{-1} in the spectrum of DBA is therefore assigned to this conformation.

The *s-trans*, *trans* conformer should have the C=O frequency which is lower by 16 cm^{-1} than that of the *s-trans* benzylideneacetophenone which becomes 1632 cm^{-1} ($1648 \text{ cm}^{-1} - 16 \text{ cm}^{-1}$). The absence of such a band in this region revealed the nonexistence of this conformer. It may be due to the sterically-hindered structure of this form. This is evident from the framework model of DBA

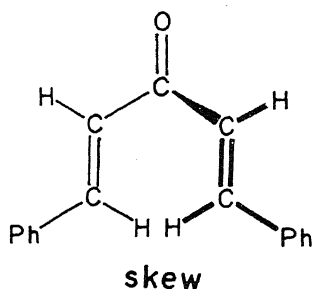


Figure 2. The skew conformation of the *s-trans*, *trans* form of DBA.

which showed significant steric interaction between the two β -H atoms and possibility of π -electron repulsion between the two C=C bonds which are sufficiently close. From these considerations it is believed to have a skew conformation so as to minimise the steric and π -electron repulsions (figure 2).

In this conformation, conjugation of the second *s-trans* C=C is greatly inhibited and the frequency of this conformer is expected to be closer to that of *s-trans* benzylideneacetophenone (1648 cm^{-1}). The inflexion observed at 1650 cm^{-1} is therefore attributed to the nonplanar *s-trans*, *s-trans* (skew) conformation.

3.1 Solvent effect

The frequencies and intensities of all the C=O bands are markedly affected by the solvents. The frequencies of the bands in CH_2Cl_2 and CHCl_3 are lower as compared to those in CCl_4 . The solvent shifts are in the order $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3$. In CCl_4 the intensities of the C=O bands are in the order *s-cis*, *trans* > nonplanar *s-trans*, *trans* > *s-cis*, *cis*. The intensity changes of the bands are quite significant. With increasing polarity of the solvent, there is a progressive decrease in the intensities of the C=O (*s-cis*, *cis*) and C=O (*s-cis*, *trans*) bands while the intensity of the C=O (skew) band increases. It is of interest to note that on passing from CCl_4 to CH_2Cl_2 the intensities of the bands of *s-cis*, *trans* and skew are reversed (figure 3).

From this it is clear that the skew form is more stable in solvents of greater polarity while *s-cis*, *cis* and *s-cis*, *trans* forms are more stable in nonpolar or less polar solvents. This is consistent with the fact that more polar forms are stabilized in more polar solvents and less polar ones in lower or nonpolar solvents.

Amongst the three conformers the *s-cis*, *cis* form is the least polar as the two C=C dipoles oppose the C=O dipole. The skew form (or *s-trans*, *trans*) is the most polar form as the C=O dipole is reinforced by the two C=C dipoles. In the *s-cis*, *trans* form the dipole of one C=C reinforces the C=O dipole and the dipole of other C=C is opposed to it. The dipole moment of this is expected to be midway between the dipole moments of the above two forms. This is evident from the dipole data (Bentley *et al* 1949) of the different conformers (figure 1).

3.2 Conformations of the DBA and their stabilities

From the intensities of the C=O bands of the three conformers of DBA in CCl_4 it is clear that the populations of these conformers are in the order *s-cis*,

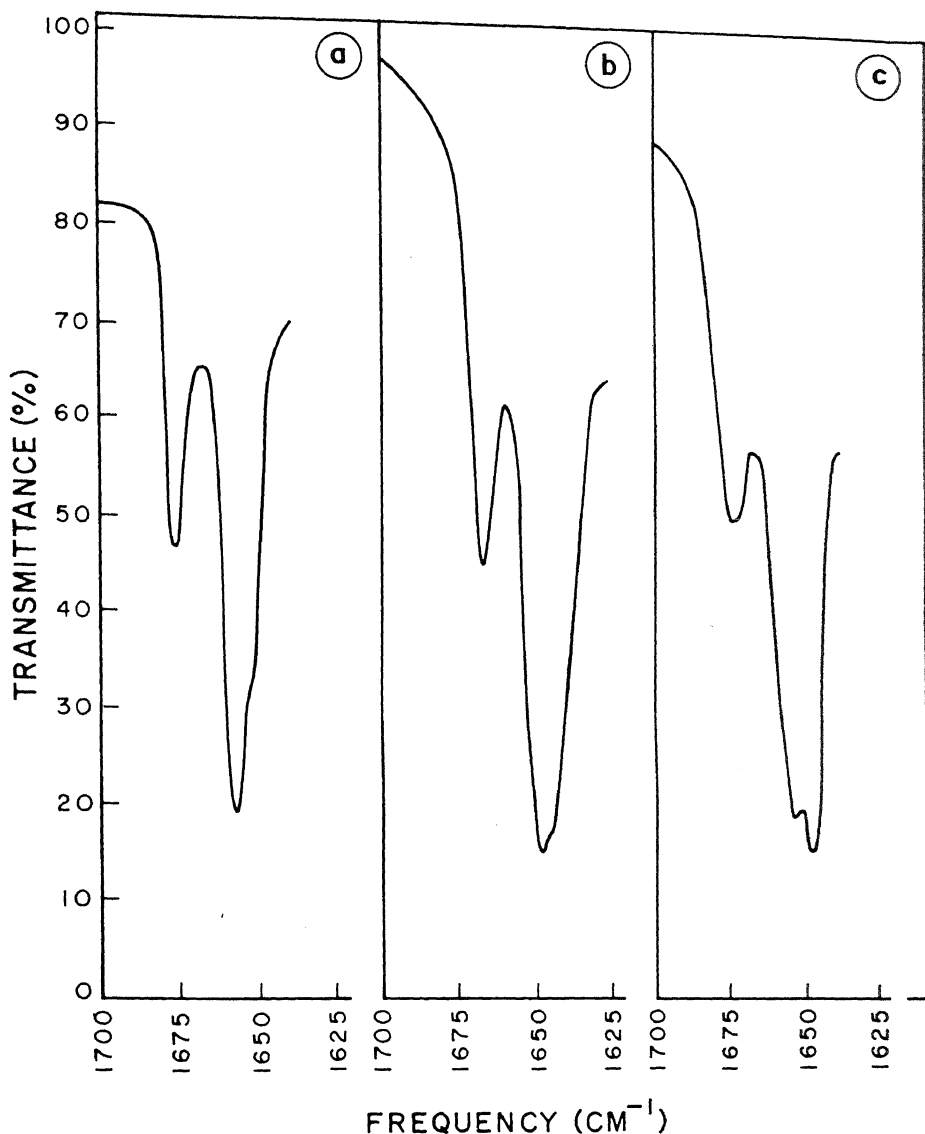


Figure 3. The C=O bands of DBA in different solvents. (a) CCl_4 , (b) CHCl_3 , (c) CH_2Cl_2 .

trans > nonplanar *s-trans*, *trans* > *s-cis*, *cis*. The lowest proportion of the *s-cis*, *cis* form may be due to greater destabilization caused by stronger repulsion between π -electrons of the C=O and two C=C bonds. The π -electron density of the C=O in this form is higher which is evident from the high C=O frequency. Of the two forms viz. *s-cis*, *trans* and nonplanar *s-trans*, *trans* the latter is less stable than the former, probably due to decrease in the resonance stabilization energy owing to the nonplanarity of this conformation.

Acknowledgements

One of the authors (GV) is thankful to the Department of Atomic Energy, Government of India, for the award of a fellowship. The authors wish to express their grateful thanks to Prof. T Navaneeth Rao for his kind help and constant encouragement as well as to the Head of the Department of Chemistry.

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